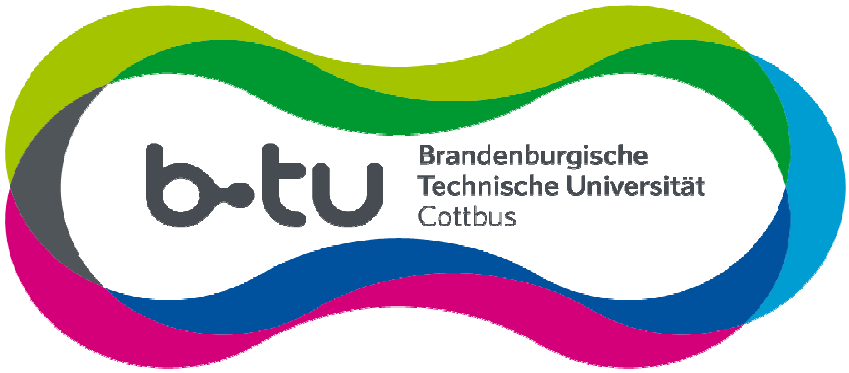

Processing and refinement of biogenous residues from agricultural, industrial and biotechnological processes

Aufbereitung und Veredlung von biogenen Reststoffen aus landwirtschaftlichen-, industriellen- und biotechnologischen Prozessen

Der Fakultät für Umweltwissenschaften und Verfahrenstechnik an der Brandenburgischen Technischen Universität Cottbus vorgelegte Habilitationsschrift zur Anerkennung der Befähigung für Forschung und Lehre

Vorgelegt von
Dr. rer. nat. Satyanarayana Narra (aus Hyderabad, Indien)

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Gutachter: Prof. Dr. -Ing. habil. Peter Ay, Brandenburg University of Technology Cottbus-Senftenberg, Germany
Gutachter: Prof. Dr. Prakash Chidanandappa Naganoor, Vijayanagara Sri Krishnadevaraya University, Karnataka, India
Gutachter: Prof. Dr. Ralf Pude, Rheinische Friedrich-Wilhelms-Universität Bonn, Germany
Gutachter: Prof. Dr. Dr. h. c. (NMU Dnepropetrovsk) Michael Schmidt, Brandenburg University of Technology Cottbus-Senftenberg, Germany
Gutachter: Prof. Dr. rer. nat. habil. Gerhard Wiegleb, Brandenburg University of Technology Cottbus-Senftenberg, Germany

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List of selected relevant publications

Agricultural residues: Cereal straws

Publication 1 **Narra, S.; Glaser, C.; Gusovius, H-J.; Stollberg, C.; Ay, P. (2011):** Agricultural residues as a renewable source of bio-energy with special focus on cereal straws. In. Zaikov G E, Pudel D P, Spychalski G. (Eds.) Renewable Resources and Biotechnology for Material Applications, (NAROSSA – 2010). Nova Publishers, Book chapter 8, ISBN: 978-1-61209-521-9, Pages 67 – 79.

Publication 2 **Narra, S.; Glaser, C.; Ay, P. (2011):** Abrasion and strength of biomass pellets as main mechanical stability characteristics. 19th European Biomass Conference and Exhibition, Berlin, Germany, 6 - 10 June 2011. ISBN: 978-88-89407-55-7, Pages 1947 – 1951.

Publication 3 **Narra, S.; Tao, Y.; Glaser, C.; Gusovius, H-J.; Ay, P. (2010):** Increasing the calorific value of Rye straw pellets with biogenous and fossil additives. Energy and Fuels, 24 (9), 5228-5234.

Industrial residues: Black liquors (lignin)

Publication 4 **Narra, S.; Ay, P.; Glaser, C.; Logsch, F. (2012):** Verfahren zur Herstellung von wasserunlöslichen Lignin-Agglomeraten. Patent-Nr. 10 2012 102 327.1

Publication 5 **Narra, S.; Logsch, F.; Glaser, C.; Ay, P. (2012):** Sludge-pelleting of paper and pulp residue. XXVI International Mineral Processing Congress "Innovative Processing for Sustainable Growth", New Delhi, India, 24-28 September 2012.

Publication 6 **Narra, S.; Ay, P. (2012):** Verfahren zur Herstellung von säurebeständigen Biopolymer-Lignin-Membranen. Patent-Nr. 10 2012 109 802.6.

Biotechnological (Biogas) residues

Publication 7 **Narra, S.; Glaser, C.; Ay, P. (2012):** Verfahren zur Herstellung von Lanzeitdünger aus Gärresten mittels Verkapselung. Patent-Nr. 10 2012 106 610.8

Publication 8 **Narra, S.; Bhandari, P.; Glaser, C.; Ay, P.; Bischof, H.; Busch, G. (2011):** Pelletisation of biogas residues with pelleting discs. 19th European Biomass Conference and Exhibition, Berlin, Germany, 6 - 10 June 2011. ISBN: 978-88-89407-55-7, Pages 1937 - 1941.

Abstract (English)

The significance in the production of bio-based products is enhanced with the abundance and renewability of biogenous raw and residue materials in comparison to the depleting fossil fuels especially in producing environment friendly products and their applications in energy (CO_2-neutral) as well as material applications. This work concentrates mainly on the production of bio-based products through innovative processing and refinement of biogenous residues originating from agricultural (cereal straws), industrial (lignin from black liquors) and biotechnological (biogas residues) processes. The innovative processing and refinement of the processes and their end-products solve the challenges which were not possible within the conventional processes. The innovative processes improve the cascading as well as sustainable utilization possibilities with a simultaneous value addition of the residues.

Converting biogenous residues into a valuable end-product requires various preprocessing of the raw materials and are material specific (physical and chemical compositions). Agglomeration of theses residues is chosen as one of the main innovative processes making the handling of the products easier. Agglomeration in this work is carried out using press / densification processes in case of cereal straws, build-up processes in case of black liquors and encapsulation processes in case of biotechnological residues.

Agricultural residues (cereal straws) are densified (press agglomeration) with the aim of producing biomass pellets and biomass mix pellets with additives, which can withstand regular handling stresses and exhibit high densities with uniform size and shape. Physical properties, such as particle size distribution after comminution is of highest importance for the binding mechanisms in the pelletisation process. Durability and strength of the pellets play an important role indicating the ability to withstand handling stresses. Particle size distributions of the cereal straws (rye and wheat) after specific comminution (using hammer / impact mill) and liberation (using twin-screw extrusion) processes have been carried out with the help of three different image analyses (Microscope, Camsizer and Fibreshape). Densified pellets are prepared with increasing water contents (from 14 wt. % to 20 wt. %) and with biogenous (paraffin: 4.68 wt. %, palmitin: 6.01 wt. %) and fossil fuel (lignite: 21 wt. % and 34.21 wt. %, anthracite: 12.16 wt. %) additives. The biogenous and fossil fuel additives are used to increase the heating values of the straws from 17.2 MJ kg^{-1} to a value in between 18.0 MJ kg^{-1} and 18.5 MJ kg^{-1} equal to the heating value of wood. The durability of the produced pellets is investigated with quadratic (standard ASAE S269.4) and octagonal (standard SS 187120) crates. Further the strength as a durability supporting parameter is measured with the help of a compression and tension testing machine (Zwick Roell type: ZMART.PRO). The particles size results showed differences in both length and width after different comminution and liberation processing. An exact comparison between the particle size analyses with the three different image analyses was not possible. The particle size distribution displayed approximately 40 % of fines and 60 % of fibers. The particle size distribution displays a direct relation to the durability of the pellets.

The particle size distribution and the different comminution and liberation processes displayed influences on the durability and strength of the produced pellets. The produced pellets with increasing water contents result in an optimum of 17 wt. % and 18 wt. % water contents measured with durability. The durability measured with quadratic and octagonal crates shows a co-relation of 1:2. The strength results show similarities to the durability results. Further this work correlates durability and strength of the pellets and discovers a positive correlation (decrease in strength with decreasing durability) between both the parameters and suggests that the strength parameter has to be provided to the consumer along with other parameters. This additional strength parameter would increase the reliability of the data especially on the quality of pellets. Particle size characteristics, durability, strength and chemical analyses show a good co-relation with each other and display optimal combustion characteristics.

Industrial residues (black liquors mainly containing lignin) are obtained as a sludge residue from pulp and paper industries. Lignin is a renewable fuel with a high heating value equivalent to anthracite coal, low ash content and hydrophobic properties. The extracted black liquors in paper and pulp mills are usually burnt at the mill directly to cover the energy production costs of the mill. The efficient utilization of lignin can reduce the percentage of lignin sludge used for energy production in comparison to the present situation. Presently the lignin is burnt / incinerated as sludge with minimum of 30 to 70 wt. % moisture content. This high moisture content reduces the energy efficiency and simultaneously utilizes a higher amount of lignin sludge in producing the required energy. Further the direct material application of black liquors and their handling are limited due to the presence of toxic cooking chemicals and heterogenic characteristics (hydrophilic / hygroscopic). Recent developments in the paper and pulp mills is to separate lignin using acidification process and agglomerate the obtained cake (30 wt. % moisture content) in to pellets. The separation process is tedious due to the particle size of lignin ranging in between 20 µm to 80 µm (low filtration efficiency) and the dried particles create a risk of dust explosion. Press agglomeration is carried out to avoid the risk of dust explosion. The produced pellets are then incinerated.

This work integrates the innovative build-up agglomeration processing using a spray-granulation process into the black liquor treatment and reduces the number of process steps required. The innovative process consists of i) production of black liquor agglomerates (granules) by spray drying, ii) acid treatment of the granules with H_2SO_4 / CH_3COOH at different temperatures and iii) warm water washing. Optimum acid treatment temperature for calcium and sodium lignin sulphonate with H_2SO_4 was found to be 130 °C, whereas the optimum acid treatment of kraft lignin with CH_3COOH was found to be 21 °C.

The acid treatment of black liquor granules lead to re-modification of the lignin structure (from soluble to insoluble) and change from a hydrophilic / hygroscopic state to a hydrophobic state. The acid treated granules are washed with warm water removing the adherent acids and salts resulting in a simultaneous increase in purity of lignin. The lignin granules are hydrophobic indicating the re-modification of their structure.

The particle size of the granules measured before and after the acid treatments are ranging in between 300 µm and 1000 µm, which indicates that the granules can be easily handled without explosion risks (which occurs at particle sizes ranging from 10 µm to 100 µm). The hydrophobic granules production with the innovative process improves the filtration efficiency, handling characteristics, reduces explosion risks and regains its original structure. Further the innovative process results in a better lignin yield compared to that of the conventional process.

The modification of the acid treatment process with the help of geometrically pre-defined filtration capsules results in the formation of briquettes due to melting and bridging of black liquor granules. The chemical analyses (elementary analyses) of the produced granules show a high reduction in sulphur and ash contents, whereas the produced briquettes show an increase in sulphur and ash contents. The reduction of sulphur and ash contents in granules is due to efficient warm water washing and their increase in briquettes is due to the inefficient cleaning of impurities (cooking chemicals and salts) in the warm water washing process step. The heating values of the produced granules are ranging from 25 MJ kg^{-1} to 33 MJ kg^{-1}. A reduction in heating value of the briquettes is observed, which is due to the containment of impurities. The innovative agglomeration techniques would lead to an optimal utilization of lignin for energy and material applications. The innovative process solves also the problem of handling, storage and explosion risks of lignin when compared to the present situation.

The production and usage of biogas from **biotechnological processes** has shown a very good potential in the last decade. Due to the increasing installations of biogas production plants, the amounts of residues from these plants are also increased. These residues from biogas plants can be used as potential fertilizers. The biogas residues as fertilizers improve the sustainability and reusability of materials in comparison to the commercial fertilizers available in the market and are helpful in reducing CO_2 and N_2O emissions. Agglomeration of biogas residues requires more understanding with respect to the physical and chemical properties of the substrates used. The characteristics of the biogas residues vary depending on the substrate and substrate mixtures utilized. Each biogas plant generates huge amounts of residues with varying characteristics. The characteristics of residues display its suitability as a liquid fertilizer. The fertilization is generally done in the growing seasons and during the winter season this liquid fertilizer creates problems in storage, handling and transportation due to the presence of high percentage of water (80 to 95 % depending on substrate). These problems can be overcome by means of agglomeration. Especially the increased use of renewable raw materials for biogas production results in an increase in fiber and solid contents of the biogas residues. The solids of digestate consist mainly of lignocelluloses, which is not degradable or difficult to degrade under anaerobic conditions. Agglomeration of biogas residues in the conventional process is carried out with the solid phase fibers after solid-liquid separation. This solid-liquid separation reduces the fertilizing contents (N, P, K) up to 50 % in the produced solid phase fiber agglomerates. The separated liquid is either brought into the field separately or is treated such that it can be discharged into open waters. The separation of both phases and bringing them separately into the field makes the process expensive and tedious.

This work tries to handle these problems with the help of innovative encapsulation processes. The innovative encapsulation process holds both solid and liquid phases together and releases their contents in a controlled release form. The controlled release of ingredients results in efficient long term fertilization.

Agglomeration of biogas residues is carried out with different additives and binders with the help of pelleting discs. Further encapsulation is carried out with polylactic acid (PLA) foils and gelatin capsules (GC). The binder CMC results as the best binder producing stable agglomerates (low abrasion and high strength) binding both solid and liquid phases together and are retaining 50 % of the nutrients (nitrogen and ammonium) useful in fertilization. The binder gelatin results in lower stable agglomerates retaining high amounts of nutrients (up to 90 %). The encapsulated capsules showed almost 100 % containment of nutrients.

This works demonstrates that innovative processes can increase the yields of different biogenous residue materials in a meaningful way. Conventional processes are improved, bio-residue utilization is increased and the sustainability of the materials is made more efficient through cascading utilization.

Abstrakt (Deutsch)

Die Bedeutung biobasierter Produkte nimmt durch die Verfügbarkeit und Nachhaltigkeit biogener Roh- und Reststoffe, im Gegensatz zu schwindenden fossilen Rohstoffressourcen stetig zu. Dies zeigt sich insbesondere im Hinblick auf die Produktion von umweltfreundlichen Produkten und deren stetig wachsenden Anwendung sowohl im energetischen als auch im stofflichen Bereich.

Im Rahmen der vorliegenden Arbeit werden innovative Verarbeitungs- und Veredlungsmethoden für biogene Reststoffe aus landwirtschaftlichen, industriellen und biotechnologischen Prozessen entwickelt, vorgestellt und bewertet. Durch die Integration innovativer Verarbeitungs- und Veredlungstechnologien können vielfältig anwendbare Produkte mit verbesserten und neuen Eigenschaften (physikalische und chemische Eigenschaften) erzeugt werden. Die vorgestellten innovativen Verfahren tragen wesentlich zur Lösung herkömmlicher Handlings-, Anwendungs- und Prozessprobleme bei. Damit tritt außerdem eine Verbesserung der Kaskadennutzung sowie der nachhaltigen Verarbeitung biogener Roh- und Reststoffe ein, was zu einer Erhöhung des Produktwertes entlang der Wertschöpfungskette führt.

Für die Erzeugung hochwertiger Produkte basierend auf biogenen Reststoffen sind verschiedene stoff- und materialspezifische Verarbeitungsschritte notwendig. Schwerpunkt in dieser Arbeit bilden innovative Agglomerationsverfahren mit denen die Produkteigenschaften biogener Reststoffe verbessert werden. Für die Verarbeitung landwirtschaftlicher biogener Roh- und Reststoffe wurden Verfahren der Pressagglomeration ausgewählt. Die Erzeugung von Ligninagglomeraten erfolgte mittels Aufbauagglomerationsverfahren. Für die Verarbeitung biotechnologischer Reststoffe kamen Verkapselungsverfahren zum Einsatz.

Landwirtschaftliche Reststoffe (Getreidestroh) werden zur Herstellung von Biomassepellets und Biomassemischpellets unter Zugabe von Zusätzen eingesetzt. Ziel ist die Erzeugung stabiler Pellets mit regulärer Form und Abmessung, welche den herkömmlichen Belastungen durch Transport- und Umschlagprozesse standhalten. Die Pelletierung erfolgt mittels Pressagglomerationsverfahren, wobei zur Verbesserung mechanisch-physikalischer und brennstofftechnischer Eigenschaften in den Pelletierprozess variable Zuschlagstoffe in verschiedenen Anteilen zugegeben werden.

Wichtige physikalische Parameter für die Erzeugung stabiler Pellets sind die Korngrößenverteilung und der Wassergehalt der Einsatzprodukte. Diese spielen eine wesentliche Rolle für die beim Verdichtungsprozess zu aktivierenden Bindemechanismen. Die Korngrößenverteilung der verschiedenen Einsatzprodukte (Roggen- und Weizenstroh) nach der Zerkleinerung in einer Hammermühle bzw. der Zerfaserung in einem Doppelschneckenextruder werden mit drei verschiedenen Bildanalyseverfahren (Mikroskop, Camsizer, FibreShape) bestimmt. Um den Einfluss des Wassergehaltes auf die Pelletfestigkeit zu untersuchen, wird das Stroh mit steigendem Wassergehalt (von 14 Gew. % bis 20 Gew. %) agglomeriert.

Zur Erhöhung des Energiegehaltes der Pellets kommen sowohl biogene Zusatzstoffe (Paraffin: 4,8 Gew. %, Palmitin: 6,01 Gew. %) als auch fossile Zusatzstoffe (Braunkohle: 21 Gew. %, Steinkohle: 12,16 Gew. %) zum Einsatz. Ziel ist die Anhebung des Heizwertes von 16 – 17 MJ kg^{-1} (Stroh) auf Werte im Bereich 18 MJ kg^{-1} bis 18,5 MJ kg^{-1}, was dem Heizwert von Holzpellets entspricht.

Die Bestimmung der Abriebfestigkeit der erzeugten Pellets wird mit zwei Teststandards (1. Standard ASAE S 269.4; 2. Standard SS 18712) durchgeführt. Die Verfahren nutzen eine quadratische bzw. achteckige Testbox mit Einbauten (Prallblech) in denen die Pellets einer Sturz- und Prallbeanspruchung unterzogen werden. Weiterhin wird von den Pellets die Druckfestigkeit mit Hilfe einer Druck-Zug-Prüfmaschine (Fa. Zwick-Roell, Type Smart.Pro) bestimmt. Die Ergebnisse der Partikelgrößenmessung zeigten Unterschiede in jeweils Längen- und Breitenverteilung in Abhängigkeit von den Zerkleinerungs- oder Zerfaserungstechniken. Die Verteilung der Korngrößen verdeutlichte, dass ca. 40 % der Partikel als fein sowie ca. 60 % als Fasern zu klassifizieren sind. Dies steht in direktem Zusammenhang zu den bestimmten Pelletfestigkeiten. Bezüglich des Wassergehaltes wird deutlich, dass für das gewählte Pressverfahren die optimale Wasserzugaben im Bereich 17 bis 18 Gew. % für die Erzeugung stabiler Pellets liegen. Der Vergleich der Messergebnisse beider Abriebtestverfahren weist eine Korrelation von 2:1 auf. Zwischen den Ergebnissen der Abriebfestigkeit und den Druckfestigkeiten der Einzelpelletprüfung kann ebenfalls ein Zusammenhang abgeleitet werden (positive Korrelation). Daraus ableitend erscheint es sinnvoll, den Parameter Pelletdruckfestigkeit als weiteren Qualitätsparameter in die entsprechenden Normen aufzunehmen. Damit wird es möglich, dem Verbraucher neben dem Parameter Abrieb zusätzliche Informationen zum Bruchverhalten (z.B. beim Transport in Förderschnecken) zur Vefügung zu stellen. Die Ergebnisse der Korngrößenverteilung, der Abriebfestigkeit, der Druckfestigkeit sowie die chemische Zusammensetzung korrelieren miteinander und weisen auf gute Verbrennungseigenschaften hin.

Industrielle Reststoffe (lingninhaltige Schwarzlaugen) sind schlammartige Produkte aus der Papier- und Zellstoffindustrie. Lignin ist ein biogener Rohstoff mit einem Heizwert ähnlich dem von Steinkohle, niedrigem Aschegehalt und hydrophoben Eigenschaften. Die Schwarzlaugen dienen in den Zellstoffwerken der Eigenenergieerzeugung und werden in Laugenkesseln verbrannt, wobei der hohe Feuchtegehalt (30 – 70 %) die Energieeffizienz vermindert und gleichzeitig dazu führt, dass eine größere Menge Ligninschlamm eingesetzt werden muss um die benötigte Energiemenge zu gewinnen. Die direkte stoffliche Nutzung von Schwarzlaugen ist bedingt durch ihre Anfallsform (hoher Feuchtegehalt, klebrige Konsistenz und den beinhalteten umwelt- und gesundheitsschädlichen Inhaltstoffen (Aufschlusschemikalien)) sowie ihren heterogenen Eigenschaften nur eingeschränkt möglich. Jüngste Entwicklungen in der Papier- und Zellstoffindustrie beschäftigen sich mit Verfahren zur Abtrennung des Lignins aus den Schwarzlaugen durch Säurebehandlung (Flockungsprozesse), Filtration der Ligninflocken und anschließender Pelletierung des Filterkuchens mit Feuchtegehalten bei ca. 30 Gew. %. Die erzeugten Ligninpellets werden energetisch genutzt.

Abstract

Im Rahmen dieser Arbeit wird im ersten Prozessschritt das innovative Sprühgranulationsverfahren zur Erzeugung von Schwarzlaugengranulaten integriert und verringert damit die Anzahl der notwendigen Prozesschritte. Der innovative Prozess besteht aus der i) Produktion von Schwarzlaugeagglomeraten (Granulaten) durch Sprühtrocknung, ii) Säurebehandlung der Granulate mit H_2SO_4 / CH_3COOH bei unterschiedlichen Temperaturen, iii) anschließendem Waschprozess mit warmen Wasser. Die optimale Temperatur zur Säurebehandlung von Granulaten aus Kalzium- und Natrium-Lignin-Sulfonat mit H_2SO_4 wird mit 130 °C ermittelt, während die optimale Temperatur für die Säurebehandlung der Kraftligninagglomerate mit CH_3COOH bei 21 °C liegt.

Die Säurebehandlung der Schwarzlaugengranulate führt zu einer Re-Modifikation der Ligninstruktur (von lösbar zu unlösbar) und einem Wechsel vom hydrophilen/hygroskopen Zustand zu einen hydrophoben Zustand. Der sich an die Säurebehandlung anschließende Waschprozess hat das Ziel, die den Granulatoberflächen anhaftenden Säuren und Salze zu entfernen und die Reinheit des Lignins zu erhöhen. Durch den Prozessschritt der Sprühagglomeration können Granulate im Korngrößenbereich von 300 µm und 1000 µm erzeugt werden. Diese Größenklassen sind ohne Explosionsgefahr (10 µm – 100 µm) handhabbar. Der vorgestellete innovative Prozess ermöglicht die Herstellung hydrophober Granulate mit wesentlich verbesserten Handlingseigenschaften (Verbesserung des Transport- und Lagerverhaltens, Ausschluss der Staubexplosionsgefahr). Außerdem wird durch den innovativen Prozess eine bessere Ligninausbeute gegenüber dem konventionellen Verfahren erreicht.

Die Modifizierung des Säurebehandlungsprozesses mit der Hilfe von geometrisch definierten Filtrationskapseln in welche die Ligningranulate vor der Säurebehandlung eingefüllt werden, führt zur Herstellung von Briketts, bedingt durch die Ausbildung von Festkörperbrücken zwischen den Einzelpartikeln und durch überlagerte Anschmelzprozesse (Teilverflüssigung der Partikeloberfläche und anschließende Verklebung der Einzelpartikel). Die chemische Analyse (Elementaranalyse) der hergestellten Granulate zeigt eine starke Verringerung des Schwefel- und Aschegehalts. Demgegenüber weisen die Briketts einen Anstieg des Schwefel- und Aschegehalts auf. Ursache hierfür ist die Effizienz des Waschprozesses. Während die an den Granulatoberflächen anhaftenden Verunreinigungen und Salze gut zugänglich und damit entfernbar sind, werden bei der Brikettbildung diese in die Brikettstruktur eingeschlossen, was einem effizienten Waschprozess entgegen wirkt. Die Heizwerte der hergestellten Granulate liegen zwischen 25 MJ kg^{-1} und 33 MJ kg^{-1}. Der Heizwert der Briketts liegt bedingt durch die Verunreinigungen etwas niedriger. Durch die innovative Agglomerationstechnik sowie die sich anschließende Säurebehandlung können Ligninprodukte erzeugt werden, die optimale für eine energetische und stoffliche Nutzung einsetzbar sind. Der innovative Prozess löst gleichzeitig die Probleme der Handhabung, Lagerung und des Explosionsrisikos von Lignin.

Abstract

Die Erzeugung und Nutzung von Biogas aus **biotechnologischen Verfahren** hat in den vergangenen Jahren stark zugenommen. Damit einhergehend ist die Menge an Biogasrückständen stetig angewachsen. Biogasrückstände können potentiell als Düngemittel eingesetzt werden. Die Nutzung von Biogasrückständen als Düngemittel besitzt im Vergleich zu kommerziellen mineralischen Düngemitteln eine höhere stoffliche Nachhaltigkeit und Wiederverwertung und tragen zu einer Reduzierung von CO_2 und N_2O Emission bei.

Die chemisch-physikalischen Eigenschaften der Biogasrückstände variieren je nach den eingesetzten Substraten und Substratmischungen, was sich in der Zusammensetzung, den Eigenschaften und der Düngewirkung widerspiegelt. Besonders der erhöhte Einsatz von nachwachsenden Rohstoffen in der Biogasproduktion führt zu einem höheren Anteil an Fasern und Feststoffen in den Biogasrückständen. Die Feststoffe in den Gärresten bestehen hauptsächlich aus Zellulose welches nur schwer abbaubar ist und sich nur bedingt unter anaeroben Verhältnissen zersetzen lässt.

Herkömmlich werden die Biogasrückstände einer Fest-Flüssig-Trennung unterzogen. Das Restwasser wird entweder als Flüssigdünger ausgebracht oder nach entsprechender Reinigung in den Vorfluter eingeleitet. Düngung wird generell in der Wachstumsperiode (Frühjahr, Sommer) durchgeführt, während in der Wintersaison ein Ausbringeverbot besteht. Damit stellen die Gärreste ein Problem bezüglich der Lagerung, Handhabung und Transport aufgrund ihres hohen Wassergehalts (80 bis 95 %, abhängig vom Substrat) dar. Die gewonnene Feststoffphase wird konventionell einer Pressagglomeration zugeführt. Durch die vorangegangene Fest-Flüssigtrennung verringert sich die Düngewirkung (durch N, P, K) um bis zu 50 % in den Agglomeraten. Insgesamt stellen sich die konventionellen Aufbereitungsprozesse als kostenintensive Verfahren dar.

Im Rahmen dieser Arbeit werden durch die Anwendung von innovativen Verkapselungsprozessen Möglichkeiten und Varianten zur Erzeugung von Düngemittelkapseln vorgestellt, in denen durch gemeinsamen Einschluss der festen und flüssigen Phase die Inhaltsstoffe erhalten bleiben. Gleichzeitig besteht die Möglichkeit einer kontrollierten Abgabe der Inhaltsstoffe, was zu einer effizienten Langzeitdüngewirkung führt.

Die Agglomeration von Biogasrückständen erfolgt in einem Pelletierteller mit dem Einsatz verschiedener Zusatzstoffe und Bindemitteln. Weiterhin werden Versuche zur Verkapselungen mit PLA Folien und Gelantinekapseln durchgeführt. Die Auswahl der Zusatzstoffe (Kalk), Bindemittel (Stärke, Gelantine, CMC), PLA-Folien und Gelantinekapseln in den Agglomeratbildungsprozess erfolgt unter den Gesichtspunkten der Bodenvertäglichkeit, biologischen Abbaubarkeit und der Einbindung beider Phasen (Fest- und Flüssigphase).

Die Ergebnisse zeigen, dass die eingesetzten Bindemittel vorteilhaft gegenüber den gewählten Zusatzstoffen sind. Das Bindemittel CMC erzielt die besten Resultate bezüglich der Agglomeratstabilität, wobei aber nur 50 % der Nährstoffe erhalten bleiben.

Mit dem Bindemittel Gelantine können bis zu 90 % der Nährstoffe erhalten werden. In den verkapselten Agglomeraten können 100 % der Nährstoffe erhalten werden. Gleichzeitig sind weniger Prozessschritte gegenüber dem konventionellen Verfahren notwendig.

In dieser Arbeit werden unterschiedliche innovative Agglomerationsverfahren dargestellt. Durch die Einbindung der innovativen Prozessschritte in bestehende konventionelle Aufbereitungs- und Veredlungsverfahren gelingt es, die Verfahren bezüglich ihrer Effizienz sowie die Produkte und Produkteigenschaften zu verbessern. Die erzeugten Produkte können vielfältig genutzt und eingesetzt werden. Damit erhöht sich die effiziente-, nachhaltige- und Kaskadennutzung von biogenen Roh- und Reststoffen.

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Symbols and abbreviations

Symbol	Abbreviation
%	Percentage
<	Less than
≤	Less than or equal to
>	Greater than
≥	Greater than or equal to
/	Or
*	Multiplication
@	At
§	Section
α	Alpha
β	Beta
γ	Binding liquid
σ_z	Tensile strength
a^{-1}	Per annum or per year
Agro	Agricultural pellet norm from France
Agro +	Agricultural pellet norm from France
ASAE	American standard
ASAM	Alkali sulphite anthrachinon methanol
approx.	Approximately
AC	Anthracite coal
Al	Alginate
BMP	Biomass mix pellets
BiomasseV	Biomasseverordnung
B	Width
Cl	Chlorine
CO_2	Carbon dioxide
CH_3COOH	Acetic acid
°C	Degree celcius
Ca-LS	Calcium lignin sulphonate

C	Carbon
CH_30	Methoxyl group
Ca	Calcium
CaO	Calcium oxide
CH_3SH	Methyl-mercaptan
CH_3SCH_3	Dimethyl sulphide
CH_3SSCH_3	Dimethyl disulphide
CH_3OH	Methanol
C_2H_5OH	Ethanol
CH_4	Methane
CHP	Combined heat and power plant
CO	Carbon monoxide
CMC	Carboxymethylcellulose
$CaCl_2$	Calcium chloride
C or conc.	Concentration
C1, C2	Centrifuge
cm	Centimeter
DIN	Deutsches Industrie Norm
D	Depth
dpi	Dots per inch
DS	Dry substance
EN	European Norm
EX	Twin-screw extruder
EC	European council
etc	Etcetera
FSG	Fließbett sprüh granulator
F	Force
g	Gram
GFP	Granule strength testing machine
G1	Glucose
G2	Maltose

G3	Maltotriose
G4	Maltotetraose
G5	Maltopentaose
G6	Maltohexaose
G	Gelatin
GC	Gelatin capsules
HM	Hammer mill
H_2SO_4	Sulphuric acid
H	Hydrogen (chemical analysis)
H_2S	Hydrogen sulphide
HNO_3	Nitric acid
Hu or Ho	Heating value
H	Height
HCL	Hydrochloric acid
h	Hours
IPCC	Intergovenrmental panel for climate change
kg	Kilogram
KL	Kraft lignin
K_2O	Potassium
kW	Kilo Watt
LS	Lignin sulphonate
L	Length
LC	Lignite coal
l	Liters
L	Lime (additive)
m	Meter
µm	Micro meter
MJ	Mega joule
mm	Millimeter
Min	Minimum
Max	Maximum

Mio	Million
MEA	Monethanolamin
MgO	Magnesium oxide
Mg	Magnesium
Min	Minutes
mol	Molecular weight
MS	Mixing system
mPa	Millipascal
ml	Milliliters
N	Nitrogen
Na-LS	Sodium lignin sulphonate
NH_3-N	Ammonium-Nitrogen
N_2O	Laughing gas
Na	Sodium
NH_4	Ammonium
NaO	Sodium oxide
NaOH	Sodium hydroxide
Na_2S	Sodium sulphide
Na_2SO_4	Sodium sulphate
NaHS	Sodium hydro-sulphide
Na_2CO_3	Sodium carbonate
NH_3	Ammonia
nm	Nanometer
N	Nitrogen (chemical analysis)
N	Newton (Force)
NaCH3COO	Sodium acetate
Nr	Number
O	Oxygen
Ö Norm	Östereichiches Norm
pH	Hydrogen potential
PCT	Polychlorinated terphenyls

PCB	Polychlorinates biphenyls
P_2O_5	Phosphorous
P_k	Capillary pressures
PLA	Polylactic acid
PGSS	Particle from gas saturated solutions
P	Pumps
PCM	Phase change materials
Pr	Quantity proportions (particle size)
P1	Straw + paraffin mixture
P2	Straw + palmitin mixture
Δp	Pressure difference
q_r	Distribution density (particle size)
Q_r	Cumulative distribution density (particle size)
r	Radius or abundances (particle size distribution)
RES	Renewable energy sources
RS	Rye straw
rpm	Rotations per minute
S	Sulphur (chemical analysis)
SS	Swedish standard
SO_2	Sulphurdioxide
S	Saturation (moisture)
ST	Spray tower
S	Starch (binder)
t	Tons
T_R	Reactor temperature
T_C	Acid treatment temperature
V	Vessel
wt.	Weight
WFD	Waste framework directive
w	Water content or moisture content
wf	Water free

waf	Water and ash free
WS	Wheat straw
XC	Carbon content
XH	Hydrogen content
XS	Sulphur content
XN	Nitrogen content
XO	Oxygen content
XA	Ash content

1. Introduction

1.1 Background

The rapid depletion of fossil fuels and the increasing demand for intensive utilisation of resources for material and energy purposes enforce the transformation of various processes concentrating on their applications for biogenous materials. Biogenous materials are produced by living organisms and are either constituents or secretions of plants or animals. Biogenous materials have to be used in a sustainable manner as they are most viable and valuable renewable resources. Viability and preciousness of these resources arise from the functionality of them as nutrition for living beings, various material processing (bioplastics, hardware, etc.) as well as energy liberation possibilities (biofuels, biogas, solid biofuels etc.) substituting fossil fuels. Presently lignocellulosic materials are the most utilized biogenic resources. The main components of lignocellulosic materials are celluloses (40 – 45 %), hemicelluloses (20 – 30 %), lignin (20 – 30 %) and extractives (2 – 5 %) (Dhepe et al., 2008). Lignocelluloses materials find their applications in different industries (woodworking, pulp and paper, fibres, chemicals, medicinal, etc.) due to their versatility (Ulber et al., 2011).

The benefits of biogenous materials utilization are that they are highly available throughout the world having environment friendly characteristics such as (i) reduction in green house gas emissions (ii) eco-compatibility, (iii) biodegradability, (iv) durability, (v) low toxicity and can be (vi) easily recycled. Process residues can be utilized further by following the cascading / recycling utilization system. The cascading utilization of residues increases the material utilization efficiency and simultaneously reduces the demand for fossil fuels and biogenous resources.

Residues are the materials left over after a certain process. Biogenous residues are the left over materials from different bio-based processes and are presently considered as most promising resources (Gokcol et al., 2009) for their further utilization. The further utilization of these residues for different purposes (fodder, feedstock, fibre, bioenergy, fertilizer, quality management, ecosystem balance, etc.) are site specific and have to be critically and objectively assessed.

Though thousands of tonnes of biogenous residues are turned out annually, none of them were harnessed with significant importance. The annual availability of these residues (husks, shells, straws, saw dust, dung's, black liquors, biogas residues, etc.) is comparatively high, which has been ignored for decades and in the recent past have gained attention due to the sky rocketing of fossil fuel prices. Currently there is a tremendous interest in utilizing these residues throughout the world and they are playing a very important role in mitigating greenhouse gases, improving resource usability, efficiency and adding value to material. The idea of utilizing residues from different biomass sectors as primary or secondary resources is considerably attractive (Wilaipon, 2008) as they are readily available, indigenous and environmental friendly.

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The problems / challenges with biogenous materials and their residues are the requirements of optimized processes and the optimal utilization of the residues. The optimization of the process can only be achieved by refinement of the material using innovative processing technologies. Refinement (beneficiation) is the upgrading process of the materials improving their material characteristics, handling characteristics (storage, transportation), etc.

The aim of innovative processing and refinement of the materials and their residues is to save handling costs, reduce wastage of materials, improve efficient utilization and sustainable management of the resources from beginning till end of the cascading process stages. Further the sustainability can be improved when residues are utilized to their maximum extent after refinement. The complete sustainable optimization process would preferably work in the form of a closed cycle, through which the major environmental risks created by fossil fuels (open cycle) can be reduced.

The residue materials depending on their physical and chemical characteristics in the refinement process have to undergo different processing steps such as liberation, separation, comminution, mixing, agglomeration, characterization (physical, chemical, mechanical, energy, etc.) and the quality control of the end product. The refined products are then transported to the end-user.

Agglomeration (build-up or press) is one of the innovative technological processes utilized in the refinement of biogenous residue materials. Agglomeration may be defined as the transformation of physical properties of the material and chemical properties of the material mixture by adding additives and transforming the fine granulometry and low density matter into solids with higher bulk density, steady shape and size utilizing mechanical pressures (Mediavilla et al., 2010).

Agglomeration is employed in many industries to produce a more durable substance (agglomerates) from loose materials enhancing the materialistic and handling characteristics such as (i) facilitating storage, transport and handling; (ii) combining a number of substances (binders and additives); and (iii) recycling / reclaiming materials (Finney et al., 2009). The primary reason for agglomeration is to improve material characteristics and their further use in technological application, increase the bulk density of the materials and reduce the handling costs.

Agglomerates of biogenous residues can be used in a broad range of applications (energy, fertilizer, fodder, litter, etc). Agglomerates are classified into granules, pellets, tablets, briquettes etc. based on their different sizes (100 µm to 20 cm), shapes (spherical, cylindrical, elliptical, rectangular, etc.) and processes (Stieß, 1997; Heinze, 2000). The particles below 100 µm are noted as dust particles.

1. Introduction

This thesis concentrates on the innovative processing and refinement of biogenous residue materials from agricultural, industrial and biotechnological processes with the help of different agglomeration techniques and produces multipurpose products (fig. 1) for various applications (energy as well as material). The different residue materials chosen from different processes are (i) stalky biomass of cereal straws as residues from the agricultural sector; (ii) black liquors (technical lignin's) as industrial residues from paper and pulp industries and (iii) fermentation (biogas) residues from biotechnological processes. These three different residue materials are chosen based on their increasing production capacities, high availability, high demand and requirement of innovative processes. Additionally the utilization of these residues with the help of innovative processes improves the cascading utilization stages and the added value of the residue product.

Figure 1 displays the three different biogenous residues in three different colours, which are i) green for agricultural residues, ii) orange for industrial residues and iii) blue for biotechnological residues. Figure 1 at the same time also displays the various challenges and their conventional processes solving the constraints (improved handling) of the respective materials to a certain extent. The similarities of the chosen three different biogenous residues are the challenges imposed on their efficient further usage, indicating an imperative requirement of the conventional processes refinement. The conventional processes are satisfying the present needs without solving all the challenges indicating a requirement of innovative processes with respect to the different material characteristics. Major challenges of the biogenous residue materials can be solved with the different innovative agglomeration and their subsequent treatment processes which are i) press agglomeration with or without additives for cereal straws, ii) build-up agglomeration and acid treatment of industrial residue 'black liquor', iii) various encapsulation methods for containment and release of ingredients from biogas residues (figure 1).

The different innovative agglomeration processes realized in this thesis are adapted based on the required end-product characteristics by refining the conventional processes and developing new processes. The new developed processes and the thus produced end products resulted in highly practical, suitable, convenient, acceptable and usable multipurpose products. The produced multipurpose products were achieved optimizing and upgrading the conventional processes by reducing processing stages and simultaneously increasing the added value of the produced products.

The different challenges in handling and producing multipurpose products from the chosen residues are elucidated separately with the modification / supplementation of conventional processes and developing new innovative processing and refinement processes individually below. Further the innovative agglomeration methods and their produced products are highlighted and discussed in individual chapters (chapters 3, 4 and 5). The innovative produced products are compared with the conventionally produced products in chapter 6.

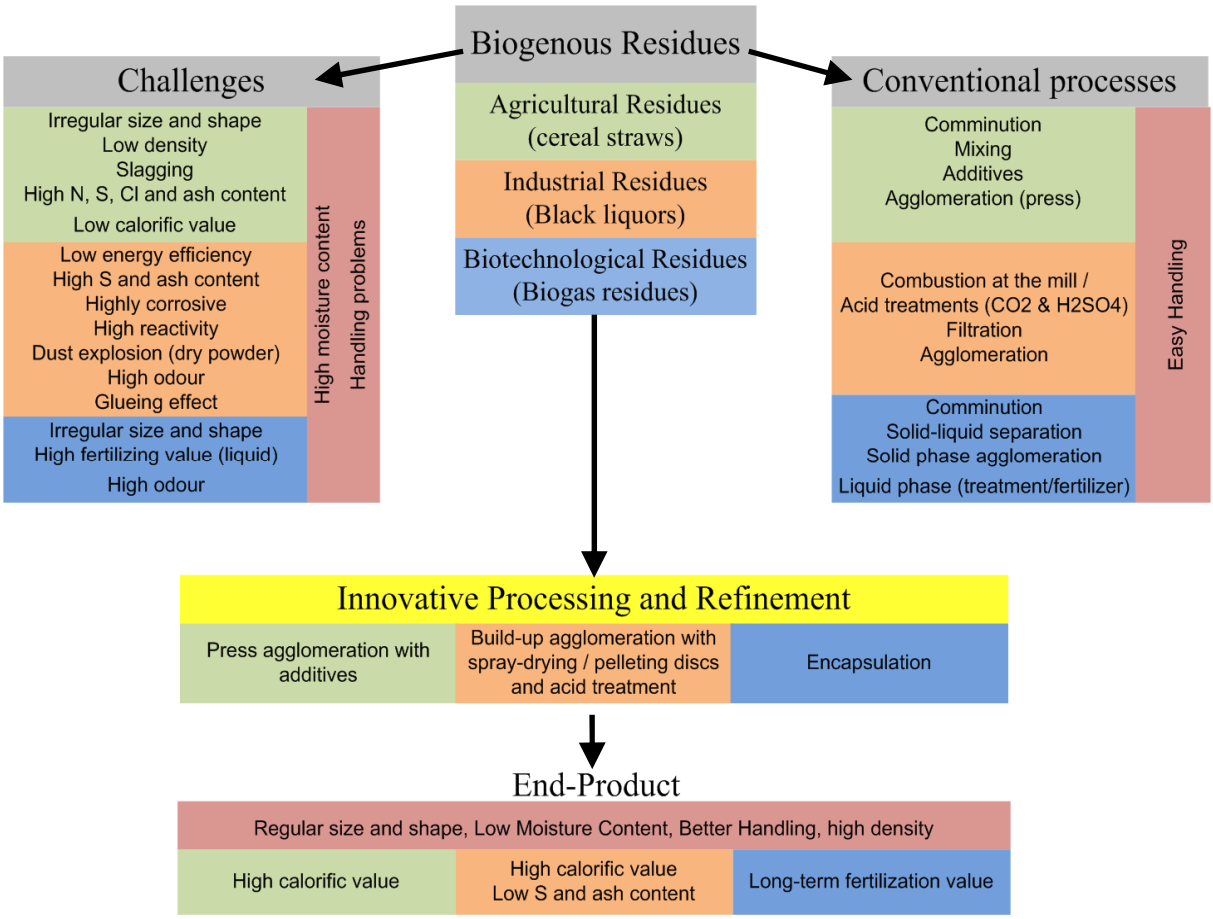


Figure 1: Schematic description of the processing and refinement of different biogenous residues and producing multipurpose products for various applications.

(i) Agricultural residues: Cereal straws (publications 1 to 3)

The use of stalky biomass residues (cereal straws) is a promising and attractive resource for material as well as energy utilization. The stalky biomass residues from cereal straws, being a widely dispersed, naturally occurring carbon resource, is considered as an efficient, economical and ecological alternative raw material for material applications as well as energy production (Klass, 1998).

Straws are generally applied in agricultural sites as i) fertilizer feeding back the ingredients into soil and helping the development of humus, ii) animal litter and as iii) animal feed. The material applications of straws are i) utilization similar to that of lignocelluloses (bio-refinery), ii) production of fibre insulation mats, iii) hardware industry, composites, etc. Further straws find their applications in different fuel production processes (solid, liquid and gaseous) involving different conversion processes.

1. Introduction

The utilization of stalky biomass residues is often difficult due to their uneven, irregular size and shape, troublesome handling characteristics (high moisture content, low density of 40 kg m^{-3}) and combustion (slagging) problems. These problems can be overcome by densification / agglomeration of loose straw materials into regular size and shape (bales).

Conventionally the cereal straws are densified in the field into cubical or cylindrical bales having a density ranging from 120 kg m^{-3} to 180 kg m^{-3}. The bales are then transported to the energy production plant and incinerated in a boiler with grate. The incineration of straw bales is up to date practiced in Denmark due to the advantages of low fuel processing stages, possibility of continuous fuel supply and relatively simple construction.

The disadvantages of this bale combustion are the restriction of bale size, shape, automatic fuel supply, non-uniform combustion, etc. Further to overcome the problems from the bales incineration process, the processes have been refined / modified using different agglomeration / densification techniques producing pellets or briquettes of cereal straws. The modified production of pellets requires different pre-processing stages such as comminution, addition of additives or binders, etc.

The densification / pelletisation / briquettisation of fibrous biomass materials after comminution are generally carried out either with high pressure compaction or with the combination of medium pressure compaction and a heating device. The main binding mechanisms in the densification process of fibrous particles under pressure are van der Waals forces, interlocking, cohesion and adhesion (Grover and Mishra, 1996).

Biomass pellets are densified biomass particles formed into pellets having defined size and shape. Pellets of various agricultural and forest residues can be used for energy production in a broad range from private household appliances to full scale power plants (Obernberger and Thek, 2009).

The application of residues in power generation has become more attractive in the recent times (DiNola et al., 2010). Co-firing of these biogenic residues with fossil fuels is already utilized to mitigate CO_2 emissions in an economically feasible way and is considered as a transitional solution in reducing global warming potentials. This research work (cereal straws) uses the principle of co-firing residues and fossil fuels as a background and prepares densified cereal straw pellets and their blends blended with biogenous and fossil fuel additives (biomass-mix-pellets: BMP). The BMP's promise great potential in enlarging the use of biomass for energy. Recently there has been an increased interest in the production of BMP's by project developers, pellet producers and energy producers. Biogenous and fossil additives are primarily selected such that they enhance the heating value of the cereal straws from 17.2 MJ kg^{-1} to a heating value equal to wood ranging between 18 MJ kg^{-1} and 18.5 MJ kg^{-1}.

Agricultural residues such as cereal straws having a hollow structure create problems in the direct combustion and bale combustion processes due to the differences in the oxygen (O) supply. The difference in O supply causes non-uniform combustion of the material, which leads to slagging in the boilers. This problem of slagging can be reduced with densification of cereal straws into pellets. The combustion of densified pellets improves the overall efficiency of the process due to their low moisture content (< 10 %) and high density (> 540 kg m^{-3}) compared to the direct incineration (moisture content > 20 %; density < 50 kg m^{-3}; slagging) of cereal straws including bales.

Biomass pellets have to undergo optimized production processes achieving high quality. The optimization of pellet quality can only be achieved as a combination of refining physical and chemical pellet characteristics. Refinement is the comprehension of densification of different particles with different sizes and shapes, hardness of pellets, temperature, moisture content, etc.

The quality of biomass fuel pellets especially from wood is evaluated based on the physical (pellet size and shape, bulk density, abrasion / durability and strength) and chemical (elements and heavy metal concentrations) characteristics of the raw materials.

The desired characteristics have been standardized in DIN 51731, DINplus, ÖNORM M 7135, EN 14961. France has suggested two additional standards (Agro+ and Agro) for pellets produced from agricultural materials (table 1). The standards Agro+ and Agro are still in the development phase. These standards are considered in the evaluation of the BMP's produced and are compared to evaluate the suitability of the produced pellets as fuel. Presently there exist no proper standards for the pellets prepared from residue materials and for BMP's.

Pellets are susceptible to high mechanical wear and tear during different handling processes producing fine particles (dust). The dust produced creates a huge inconvenience to the end-user (high ash content, health hazards, fire and explosion risks and disturbances in the automated fuel feeding system).

Abrasion and strength are the most important physical characteristics in determining the quality of pellets. Lower abrasion and higher strength indicate the development of a minimum amount of dust during the handling of pellets. A single parameter which takes both strength and abrasion of pellets into account is not known so far (Uhlemann and Mörl, 2000). This work tries to develop a correlation between abrasion and strength for the better understanding of new approaches in reducing fine particles development during the mechanical wear and tear of pellets in different processes.

Table 1: Standard quality values of the wood pellets as specified in DIN 51731, ÖNORM M 7135, DINplus, EN 14961 and for agricultural pellets Agro+ and Agro (Pelletatlas, 2009) from France.

Norms for Pellets	**DIN 51 731**	**ÖNORM M 7135**	**DINplus**	**EN 14961**	**Agro+**	**Agro**
Diameter (mm)	4 – 10	4 – 10	--	6 – 25	6 – 8	6 – 16
Length (mm)	≤ 50	≤ 5*d	< 5*d	3.15-50	10 – 30	10 – 30
Abrasion (%)	--	≤ 2.3	≤ 2.3	≤ 1-3	≤ 5	≤ 8
Heating value (MJ kg^{-1})	17.5-19.5	> 18	> 18	≥ 13.2-19	≥ 15.5	≥ 14.7
Water content (%)	≤ 12	≤ 10	≤ 10	≤ 10-15	≤ 11	≤ 15
Ash content (%)	< 1.5	< 0.5	< 0.5	≤ 3-10	≤ 5	≤ 7
Density (kg m^{-3})	> 540	> 540	> 540	≥ 600	≥ 650	≥ 650
Additives (%)	Not allowed	≤ 2	≤ 2	≤ 2-5	No limit	No limit
S (%)	< 0.08	< 0.04	< 0.04	≤ 0.04-0.2	≤ 0.2	≤ 0.2
N (%)	< 0.3	< 0.3	< 0.3	≤ 1-2	≤ 1.5	≤ 2
Cl (%)	< 0.03	< 0.02	< 0.02	≤ 0.03-0.3	≤ 0.2	≤ 0.3

The production of cereal straw pellets and their blends requires physical size reduction (comminution) processes as a pre-requisite for the compaction of fibrous particles into dense and durable pellets, improving the handling (storage and transportation) and combustion efficiencies (Adapa et al., 2007; Mani et al., 2003). The uniform size and shape of the densified pellets allows them to be easily adopted in direct-combustion or co-firing with coal, gasification, pyrolysis and in other biomass-based conversion technologies (Kaliyan and Morey, 2006).

This work produces 8 mm pellets from cereal straws (rye and wheat) and their blends. The straw has to be ground to particles having a size less than 8 mm, for producing 8 mm pellets such that the particles do not block the pellet mould (Obernberger and Thek, 2009). The size reduction of the rye and wheat straw was accomplished with the help of an impact mill / hammer mill (HM) as well as with a twin-screw extruder (EX).

(ii) Industrial residues: Black liquors (lignin) (publications 4 to 6)

Technical lignin's (black liquors) are byproducts of the pulping industry. The amount of black liquor obtained from the pulp cooking process is about 50 Mio t a^{-1} worldwide (Kamm et al., 2006) with 3 Mio t a^{-1} from sulphite pulping and 47 Mio t a^{-1} from sulphate pulping processes. Black liquors from pulp industries are either classified as lignin sulphonates (LS) or Kraft lignin (KL) depending on the pulping process and the process chemicals utilized in the cooking process.

In order to extract the pulp from the lignocelluloses in wood, cooking chemicals are added to convert the natural insoluble lignin into a water soluble form by modifying its structure. Lignin sulphonates result from sulphite pulping and Kraft lignin results from the sulphate pulping process. The pulp mainly consists of celluloses and hemi-celluloses. The black liquor is obtained as a residue after the separation of the pulp fibres. Most of the black liquor from sulphate pulping is directly burnt (Liu et al., 2009) at the pulp mill partially covering the energy requirement of the mill.

Currently the material application of black liquor is limited to less than 4 % of the total amount produced worldwide. The main component in black liquor is the biopolymer lignin along with the cooking chemicals. The black liquors are generally burnt at the pulping industries along with the wood bark directly producing the partial / total energy required for running the plant.

Only in the recent past, lignin is either separated or precipitated from the black liquor (LignoBoost Process) and is supplied for material utilization as well as energy production (Ohman et al., 2006; Ohman and Theliander, 2007; Ohman et al., 2010). The end product lignin obtained from the LignoBoost process still contains approx. 30 % moisture content (Ohman et al., 2006).

Black liquors are mainly handled in liquid form, which is highly corrosive and results in high energy efficiency losses due to evaporation. The handling of black liquor in powder form (after drying it to powder) is highly reactive and causes high fire and explosion risks. Thus black liquors are always stored with a moisture content of around 30 % to overcome the above mentioned problems. The differences in the moisture content on top and bottom of a container lead to the formation of clumps, especially for black liquors stored with an average 30 % moisture content in their storage due to dryness on top and high moisture content on bottom (Lindmann and Smaragdis, 2009). The formed clumps have high strength and these clumps require a high amount of dismantling energy. The clumps tend to block the automated feeding system of the further employed conveyor belt due to irregular sizes and shapes. To overcome the clumps formation, black liquors with 30 % moisture content have to be continuously mixed / stirred to keep it in a homogenous mixture state. These problems are currently overcome by drying the separated lignin into powder form and by densification of the lignin powder into pellets (Tomani, 2010).

The biopolymer lignin has a high calorific value ranging between 26 MJ kg^{-1} and 28 MJ kg^{-1}, which is almost equal to that of the anthracite coal (29 MJ kg^{-1}). The high moisture content (30 to 70 %) of the black liquor leads to the reduction of energy efficiency from 28 MJ kg^{-1} to about 17 MJ kg^{-1} (generally ranging in between 9 MJ kg^{-1} and 17 MJ kg^{-1}) due to the evaporation energy losses (Lindman and Smaragdis, 2009). The evaporation energy losses range in between 9 MJ kg^{-1} to 19 MJ kg^{-1} and is mainly dependent on the moisture content of the product to be incinerated. Generally the lignin product is incinerated with a minimum of 30 % moisture content resulting in an energy efficiency loss of about 10 MJ kg^{-1} (Lindman and Smaragdis, 2009).

The high sulfur content present in the black liquor demands a flue-gas desulphurization apparatus to avoid acid rain formation, this is also necessary based on the regulation guidelines given by 'Technical Instructions on Air Quality' (13. BImSchV). Further the direct utilization of black liquor for material purposes is limited due to the presence of certain toxic chemicals (cooking chemicals). The material utilization of black liquor can only be carried out after certain modification or separation processes are carried out depending on the required end product characteristics.

An innovative technological processing and refinement of black liquor is required to solve the handling / utilization problems associated in different forms (liquid, solid powder, sludge with 30 % moisture) in an efficient manner.

Several methods for precipitation of lignin from black liquor using flocculation, sedimentation and coagulation are well known (Garg et al., 2005; Zaied and Bellakhal, 2009). These processes are mainly used in the treatment of effluent waters from paper and pulp industries. These processes are carried out by reducing the black liquors pH value with the help of acids to a desired pH value, in which the lignin precipitates and can be separated. The separation or precipitation processes are accompanied with high material losses due to condensation or degradation occurrences, resulting in low purity, solubility in water, and having remains of pulping chemicals, etc (Liu et al., 2009).

An optimized flocculation / coagulation method developed in the recent years is the LignoBoost process (Ohman et al., 2006; Ohman et al., 2010). The LignoBoost process utilizes CO_2 in reducing the pH value and precipitates lignin from black liquors. This process consecutively treats the precipitated lignin with concentrated sulphuric acid (H_2SO_4) and with water washing the lignin for four or more times increasing the purity and yield of the lignin (Ohman et al., 2006; Ohman et al., 2010).

The traditional / conventional / present state of the art processes of extracting lignin from black liquor focus on an acid-treatment of the liquid liquor. The separation of lignin has been achieved with the help of subsequent filtration processes. The filtration process leads into filtration problems due to the fine particle size (fine dust ≤ 20 µm) of lignin (plugging of the filter cake, slow flow of the washing liquor through the cake) resulting in high impurities of the product (Tomani, 2010). Further these processes are highly tedious, require high amounts of acids, consume lots of energy and the costs are high.

This work tries to solve the above problems from the conventional processes using an innovative build-up agglomeration of black liquor using spray-granulation / spray-drying processes (< 100 °C) and produces appropriate agglomerates (granules). The agglomerates are then treated with acids re-modifying the lignin structure. The agglomerates produced are porous, dry, dense, having high surface area, and are having particle sizes higher than dust particles.

The granules contain mainly lignin polymer along with impurities (cooking chemicals). The impurities from granules are cleaned using the acid (H_2SO_4 or CH_3COOH) treatment process. The porous granule structure offers a large surface area for the specified acid reaction. The acid treated granules still contain some acid remaining adherent on the surface of the granules, which have to be washed away with water. The measurement of sulphur and ash content gives the evidence of impurities and their adherence on the granules.

The acid treatment of granules leads in conversion of water soluble black liquor granules into water insoluble black liquor granules regaining the original characteristics of lignin and simultaneously increasing the purity and yield of lignin. The acid treatment also modifies the structural properties of the granules. The particles inside the granule undergo melting and bridging processes co-instantaneously and develop into an encapsulated hydrophobic lignin granule.

The ligninsulphonate granules (Ca-LS, Na-LS) from sulphite black liquor treated with the acids undergo a desulphonation process by the elimination of sulphonate groups. The Kraft lignin granules with the acid treatment undergo a reduction in pH value through which it regains its original structure.

The modification of lignin granule structure from a hydrophilic to a hydrophobic form with the acid treatment and the thereafter produced granules have the following advantages such as (i) no acid losses due to the exothermic reaction of acids with water, (ii) efficient acid reaction due to high surface area of granules, (iii) reduction in the amount of acid required, (iii) increase in filtration efficiency, (iv) direct utilization of granules for material as well as for energy applications, etc., in comparison to the conventional separation of lignin from liquid black liquors through flocculation / coagulation processes.

Granules in the acid treatment process can be further modified into water-insoluble agglomerates of bigger dimensions (briquettes or pellets) with the help of a geometrically predefined volume restraining filtration device (filtration capsule). The acid treatment process of granules carried out in a filtration capsule resulted in briquette formation due to the sintering / melting and bridging of particles inside the individual granules and with the surrounding neighbor granules.

The briquettisation of black liquor granules is due to the melting and bridging of (i) highly viscous binder lignin inside the granules and (ii) development of a certain pressure inside the filtration capsule due to volume restrainment during the acid treatment process. The briquettes have revealed an increase in density (depending on the pressure development), filtration efficiency by reducing the colloids formation and through which improved the storage and handling properties.

The utilization of agglomerates (granules or briquettes) for material or energy applications has to be distinguished based on their specific characteristics. The material utilization of granules / briquettes requires high purity, whereas the energy utilization requires a stabilized size and shape, low moisture content, etc.

The granules with their spherical structure are more ideal for material applications due to their high purity, uniform size (1 to 5 mm), low odor, low sulphur content, high surface area, etc. These properties of the granules are desired in many material application processes such as bio-plastics, vanillin production, etc (Gosselink et al., 2004). The briquettes can be used for energetic applications due to high density, low water content, etc.

This work produces granules from different black liquors from sulphite (calcium-ligninsulphonate and sodium-ligninsulphonate) and sulphate (Kraft lignin) pulp cooking processes. The production of granules is carried out with the help of the spray-granulation process below 100 °C reactor temperature and refines the process by producing briquettes with the help of a geometrically predefined filtration capsules in the acid treatment process. Further this work also compares the evaporation energies and their energy efficiencies for both the conventional and the refined processes.

(iii) Biotechnological (Biogas) residues (publications 7 to 8)

Currently there is an increased utilization of residues from different biotechnological processes (Poeschl et al., 2010; DiNola et al., 2010). This utilization of biogenous resources and their residues results in a sustainable utilization of the biomass resources in different forms. This work concentrates on the innovative agglomeration and refinement through macro-encapsulation of biogas residues for their efficient long term utilization (controlled release) as fertilizers.

Biotechnology plays an important role in the replacement of fossil fuels in power and heat production as it is one of the most energy efficient and environmentally neutral energy sources (Fehrenbach et al., 2008). Biotechnological processes mainly concentrate on the fermentation of biogenous materials and produce gases (bio-gas), liquids (bio-ethanol) and process residues.

The fermentation process involves breakdown of organic matter (sewage sludge, animal manure, industrial effluents, energy plants, grasses, etc.) in the absence of oxygen. Biogas is composed of methane (50 % - 70 %), carbon dioxide (35 % - 40 %) and hydrogen sulphide (< 1 %) with trace amounts of ammonia and water vapor.

The process residues left after the anaerobic digestion of the different substrates are known as the biogas residues. The utilization of different materials and their mixtures in the biogas production process results in residues with varying characteristics. The utilization of these residues for different purposes has to be carefully taken into consideration due to their heterogeneity. The major challenges in the utilization of liquid biogas residues are handling (storage, transport) and odor problems. The direct utilization of biogas residues for any purpose is complicated due to high moisture contents (≥ 85 %) and wide range of particle sizes present.

The residues can be directly utilized as liquid crop fertilizer due to the high presence of nitrogen and potassium in the liquid as well as in the solid phase. The presence of high nitrogen and potassium contents helps in increasing the soil fertility, humus development, crop yield, replenishing the nutrient cycles and substitutes / reduces the production and utilization of commercial fertilizers (Arthurson, 2009).

Even though the utilization of fermentation residues has high potential as fertilizer, their utilization is limited due to high transport costs (due to high liquid contents) and is only economical when carried out at a regional scale (r < 35 km) (Wulf and Döhler, 2009; Teows, 2009). The fertilization in field is further limited by regulations (DüMV, 2008) stating the allotted time period for fertilization. The regulated law states that the fertilization in the field is only allowed during the spring and summer seasons of a year, indicating no fertilization in the winter season (November to January). The retention of fertilization in winter season is to avoid the excessive nutrient input and also to reduce the risk of water bodies as well as ground water contamination.

Conventionally agglomeration (fertilizer pellets) of biogas residues is carried out as a technological solution in solving the handling problems. The conventional agglomeration of biogas residues requires particle size reduction (grinding), drying / dewatering, etc. Agglomeration of biogas residues with the present state of the art technology is carried out only with the solid phase (fibres) materials after a solid-liquid separation process. The agglomeration of solid phase materials results in the loss of NH_3-N present in the separated liquid phase. The losses in NH_3-N result in the reduction of the fertilizer efficiency of biogas residues and simultaneously increase the laughing gas (N_2O) emissions development in its further processing.

The production of agglomerates / pellets from liquid-biogas residues without dewatering is only possible with specific optimized technology and refinement with or without additives. One specific optimized process of holding solid and liquid phase materials together in a single agglomerate is the encapsulation technology. The encapsulation technology is currently applied to capture active ingredients in the pharmaceutical industry. The pharmaceutical industry utilizes micro-encapsulation technologies. Basic research on the utilization of micro-encapsulation technology for biogas residues has been carried out by the company IASP GmbH in Berlin during the time period between 2002 and 2004. The researchers from IASP GmbH utilized the micro-fibre matrix from fruit residues, sugar beet corsettes, etc. The results of the research showed that up to a 50 % capture of the nutrient content in the dried end product is achievable.

The utilization of encapsulation processing technology for biogas residues requires innovative rudiment variations and the possibilities for the application of long fibres. The micro-encapsulation (< 50 µm) of biogas residues requires very fine wet comminution / grinding. The fine wet comminution / grinding is not advisable from the energy as well as economical and technical point of view. The utilization of micro-encapsulation technology for biogas residues is restricted due to its characteristics (long fibres, big particles, non-uniform particle size, high moisture content, etc).

Macro-encapsulation of biogas residues has not yet been investigated till now. This work tries to propagate the micro-encapsulation into the macro-encapsulation producing agglomerates / pellets of long fibres / big particles (1 to 10 cm in length and up to 1 cm in diameter).

The advantages of the macro-encapsulation of biogas residues are:

1) Comminution / grinding of biogas residues are not necessarily required,
2) Complete fixation of nutrient contents,
3) Reduction of laughing gas emissions,
4) Improvement of handling characteristics,
5) Long-term fertilizer effect through nitrogen fixation and due to controlled release,
6) High fertilization efficiency, etc.

1.2 Objectives / Aims

The objective of this work is to process and refine three different biogenous residue materials from agricultural, industrial and biotechnological processes.

(i) Agricultural residues: Cereal straws

The aim of this work is to investigate (i) particle size distribution of rye and wheat straws after different comminution processes with the help of three different image analysis systems (Microscope, Fibreshape and Camsizer); (ii) optimisation of water content as binding material in the pellet production; (iii) quality control of pellets with the parameters abrasion and strength; (iv) increasing the heating value / calorific value with the help of additives; (v) quality control of pellets with biogenous and fossil fuel additives (BMP); (vi) comparison of pellets abrasion with two different standards (ASAE S 269.4 and SS 187120); (vii) development of a correlation between the parameters abrasion and strength.

(ii) Industrial residues: Black liquor (lignin)

The aim of this work is to investigate the (i) production of different black liquor granules with varying reactor temperatures; (ii) particle size distribution of the produced granules using an image analysis system (Camsizer); (iii) measurement of granule strength using granule strength testing machine (GFP); (iv) treatment of granules with different acids and varying temperatures; (v) measurement of granule particle size after acid treatment; (vi) measurement of granule strength after acid treatment; (vii) production of briquettes using a volume restraint filtration device; (viii) measurement of briquettes strength, (ix) evaluation of product purity (granules as well as briquettes) based on elementary analysis.

(iii)Biotechnological (Biogas) residues

The objective of this work is (i) to measure particle sizes of the biogas residues before and after comminution with impact mills classifier sieves having aperture sizes of 10 mm and 6 mm; (ii) producing the biogas residue pellets with additives; (iii) optimization of additive mixtures for pellets formation without dewatering; (iv) densification of biogas residues after dewatering; (v) evaluation of mechanical stability of the produced pellets (strength and abrasion); (vi) production of macro-encapsulated biogas residue pellets; (vii) evaluation of the mechanical stability and nutrient (NH_3 and N) holding capacity of the macro-encapsulated pellets.

Further the produced agglomerates from the innovative and refined processes are compared with the agglomerates produced from traditional / conventional processes by describing briefly the positive and negative aspects of each individual process with respect to the chosen residue materials.

1.3 Structure of the thesis

This thesis work is dissected into five parts and will be investigating the different conventional agglomeration processes and comparing them with the innovative processing and refinement processes of three different chosen biogenous residue materials (cereal straws, black liquors and biogas residues). Further this work tries to compare the end products of both the processes (innovative and conventional).

(i) State of knowledge (chapter 2)

This chapter describes the state of the art technology relevant in processing of different biogenous materials and obtaining the different multipurpose main products along with the process residues. This chapter also enlightens on the conventional processing technology of the respective residues and their end product quality standards.

(ii) Agricultural residues: Cereal straws (chapter 3)

This chapter deals with the development of technologies for the incineration and production of high calorific value biomass pellets for energy. Investigations have been carried out over different comminution technologies, production of biomass mix pellets (BMP) with and without additives with special focus on the quality assurance as per the available standards. The discussions are mainly based on the relationship between particle size distribution after different comminution and the durability of the produced pellets. The results obtained are further compared with the specified standards to check the suitability of the produced pellets as fuel for incineration.

(iii)Industrial residues: Black liquor (lignin) (chapter 4)

This chapter deals with the development of a method for producing bio-agglomerates from pulp industry residues (black liquors) for their utilization in material as well as energy applications. Investigations on the production of granules have been carried out with a spray-granulator and the consecutive treatment of granules with acids re-modifying the structure of lignin into its original hydrophobic characteristic. Further the production of briquettes from granules in the acid treatment process with the help of a geometrically defined volume restraining device has been investigated. The discussions are mainly based on the purity and yield of lignin along with particle size distribution of granules before and after acid treatment, density of granules, density of briquettes, chemical elemental analysis measuring the impurities (sulphur and ash contents) and the development of new processes.

(iv)Biotechnological residues (chapter 5)

This chapter deals with the development of a new innovative macro-encapsulation technology to increase the short and long term fertilization effect of biogas residues through controlled release of nutrients in the soil. Investigations on the production of macro-capsules have been carried out with the build-up pelletisation process with different process approaches (with and without comminution, with and without dewatering, etc.).

The produced capsules are then compared to the traditional / conventionally produced pellets. The discussions are mainly based on the nutritional values of the produced pellets / capsules, pellets sizes, shapes and stability.

(v) Comparison of conventional and innovative processes (chapter 6)

This chapter compares the results of the conventionally produced end products with the end products produced using innovative processing and refinement processes, including advantages and disadvantages of both the processes.

2. State of knowledge

2.1 Biomass and its composition

Biomass refers to organic materials that originates from plants and animals (Kaltschmitt et al., 2009). The plant biomass stores energy from sunlight by photosynthesis in bonds of carbon, hydrogen and oxygen molecules (Ryu et al., 2006). Plant biomass is characterized into four main types: woody plants, herbaceous plants, grasses and aquatic plants (McKendry, 2002; Kaltschmitt et al., 2009). Animal biomass can be characterized either as animal slurry or as farmland manure and is categorized in wastes and residues. The animal biomass is generally used in producing gaseous fuel using fermentation processes and is also used as fertilizer in the field. Further biomass is also produced through different metabolic activities of the microorganisms. The produced microbial biomass finds its intensified use as food and fodder (Boze et al., 1995).

The total biomass, which is presently finding applications in both material and energy purposes worldwide, is about 3.1 billion tonnes annually. The utilization of biomass for material applications (52 %) is slightly dominating over that of the energy applications (48 %) (Raschka and Carus, 2012). The use of biomass as renewable resources accounts to 27 % and rest of the biomass is used in production of food (15 %) and animal feed (58 %) (Raschka and Carus, 2012). Plant biomass is essentially composed of celluloses (40 – 45 %), hemicelluloses (20 – 30 %), lignin (20 – 30 %) and extractives (2 – 5 %) (Sjöstrom, 1992). Biomass is presently estimated to contribute about 14 % of the world's total energy supply (Zhengqi et al., 2008).

The utilization of biomass resources for various purposes is considered as an environmental friendly application as it can reduce CO_2 emissions in their production and replaces / reduces the demand for fossil fuel resources. The biomass has to undergo product specific modifications based on the end-use of the specified biomass as a source of fuel (granules / pellets / briquettes in the solid fuel form, biogas in the gaseous fuel form and biodiesel / bio-ethanol in liquid fuel form) for energy purposes or as a source of material applications (hardware, feed, fertilizer, fibre, etc.). Solid fuels are prepared by densification of biomass after certain pre-processing stages. Gaseous and liquid fuels are mainly prepared by only utilizing celluloses and hemi-celluloses after separating lignin and extractives.

The separated lignin and extractives are left out as process residues. The production of these residues has increased exponentially in the past decade and will be continuing to increase in the future, as biomass is currently the most promising (viable and valuable) resource in producing different bio-fuels (gaseous and liquid). There is an increased interest in the efficient sequential utilization (cascading system) of these residues for material (animal feed, fertilizer, etc.) as well as energy (bio-char, surrogate fuel, etc) production improving the overall economy of present facilities.

2.2 Biomass and its products definitions

The term biomass as per the different energy laws is defined as follows (Thrän et al., 2011):

- Biomass including biogas as per the Renewable Energy Sources (RES) Act is defined as landfill gas, sewage sludge gas as well as the biodegradable fraction of wastes / residues from households and industry (Erneuerbare-Energien-Gesetz, 2009),
- Biomass is defined as the "source of energy from phyto- and zoomass" as per the biomass regulation (BiomasseV, 2005: Biomasseverordnung – Section (§) 2 paragraph 1) including also the resulting consequent products such as by-products, residues and wastes, whose energy content is derived from phyto- and zoomass and
- Biomass is defined as the biodegradable fraction of products, wastes and residues from biological origin from agriculture (including vegetal and animal substances), forestry economics and related industries, including fisheries, aquaculture as well as the biodegradable fraction of wastes / residues from industry and households as per the Directive 2009/28/EG.

2.2.1 Legal Definition of Biomass

According to section (§) 2 of the Regulation (BiomasseV, 2005), the following fractions of biomass are included:

- Plants and their parts,
- Energy sources produced from plants or their parts, all of the intermediate and end products from biomass as defined in BiomassV, (2005),
- Matured forest wood / timber, consisting of used wood (used products made from wood, wood products and composite materials) or industrial matured wood (hardware working wood or process wood residues), obtained as a waste, unless clause 2 in BiomassV, (2005) precludes or according to section (§) 3 number 4 it is not recognized as biomass,
    a) Containing less than 0,005 weight % of polychlorinated biphenyls (PCBs) and polychlorinated terphenyls (PCT) according to the PCB / PCT Waste Ordinance 26th June 2000 (Federal Law Gazette I, page 932), and
    b) Having less than 0.0001 weight % of mercury content.
- Paper, cardboard, textiles,
- Waste and by-products of plants and animal origin from agriculture, forestry and fishing industries,

- Animal by-products as defined in article 2 paragraph 1 of Regulation (EC) number 1774 / 2002 of the European Parliament and the Council (especially the products which are not consumable by human beings),
- Organic waste as defined in Bio-waste-ordinance (section (§) 2, number 1),
- Mixed municipal waste from private households and similar waste from other origins,
- Gas produced from matured wood as long as it does not preclude clause 3 of BiomassV, (2005) and as per section (§) 3 number 4 it is not recognized as biomass,
- Gasification or pyrolysis gas produced from biomass and the resulting secondary products and by-products,
- Biogas produced by anaerobic digestion, as long as the fermentation is not carried out with materials specified in section (§) 3 number 3, 7, and 9 of BiomasseV, (2005) or the fermentation materials are not mixed with sewage sludge having a mixture ratio more than 10 wt. %,
- Sewage sludge in accordance with the Sewage Sludge Ordinance,
- Harbor sludge and other water slurries and sediments,
- Sewage gas, landfill gas,
- Plant oil methyl ester, if not contrary to the clause 4 in BiomassV, (2005),
- Alcohols produced from biomass (BiomasseV: section (§) 2 paragraph 3) and
- Peat.

Further there are various legal definitions of biomass, which are collectively made to suit each and every discipline. Biomass is subsumed under the terms i) cultivation biomass (ex. energy crops, agricultural, forests, etc.), ii) accessible biomass (landscape residues) as well as iii) wastes, iv) residues and v) byproducts.

The waste legislation defines the main product, by-product and waste as follows:

A **by-product** under the Waste Framework Directive (IPCC, 2001: article 5, paragraph 1) is defined as a substance or matter resulting apart from the **main product** in a specific manufacturing process. A substance or matter can only be regarded as a by-product and not waste (as defined in article 3, section 1) when the following conditions are met:

a) It is certain that the substance or matter can / will be reused,
b) The substance or matter can be used directly without further processing other than in the normal industrial practice,

c) The substance or matter is produced as an integral part of a manufacturing process and

d) Further use of the by-product is legalized, i.e. the substance or matter fulfills all the relevant product, environmental and health safety protection requirements for the specified use and does not lead in adverse environmental or health consequences.

Waste is defined as a substance or matter, which the possessor either disposes or intends to dispose or is required to be disposed (article 3, section 1 of the Waste Framework Directive (WFD: IPCC, 2001). The German national standard definition of waste is given by the Recycling and Waste Act (section (§) 3 paragraph 1) as the Waste Framework Directive in the member states of Germany is dependent on the liability and transposition of the state (Dyckhoff and Spengler, 2005) and is the complete tangible / agile personal property.

The term **residue** is mentioned in various laws without specific definition and this makes the distinction between waste, by-products and residues to be vague. The Directive 2009/28/EC, states that residues have to be categorized separately distinguishing themselves from the categories of waste and by-products. Residues and waste as per the Directive have a different legal status in comparison to that of by-products. Some residues (straw, bagasse, husks, cobs and nut shells, etc.) are mentioned explicitly without any systematic distinction of residues with waste or by-products.

Biogenic residues from biomass are the by-products / residues / wastes from the present organic material flows (figure 2). Residues in this thesis considered are either the by-products or the wastes of biogenic material flows specific to each main product manufacturing / production process.

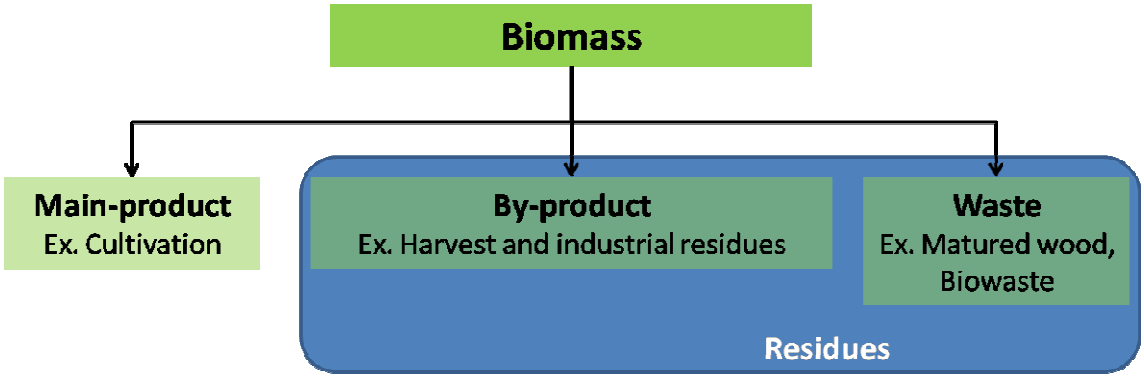


Figure 2: Definitions of residues, byproducts and wastes (Thrän et al., 2011).

2.3 Cereal straws as agricultural residue

Cereal straws represent a considerable residue potential as a valuable resource for their utilization in many processes. Germany possesses the second largest potential of cereal straws after France in the European Union producing around 37 Mio t a^{-1} (without the consideration of maize residues) (Source: bioenergie-emsland.de, last visited on 10.07.2012). The high amounts of cereal straw residue production are due to the high priority of cereals as food. 40 % of the total available straw (13 to 15 Mio t a^{-1}) can be utilized for material as well as energy application purposes after the allocation of straw for fertilizing in the field and as animal feed (Source: smul.sachsen.de, last visited on 10.07.2012).

Straw produced on arable land after the harvest of cereal grains is a by-product / residue that is usually dried in the field. Cereal straws are storable when the water content is below 18 wt. % and can be used in i) heat and electricity production, ii) 2nd generation liquid bio-fuels (bio-ethanol, biomass to liquid) production, iii) building materials, iv) fibres, v) fibre reinforced composites, vi) animal feed, vii) animal litter, viii) fertilizer, ix) raw material for chemical industry, etc. Cereal straw residues are gaining more and more importance as they can efficiently replace / reduce the demand for wood. The utilization of straw for various purposes has to be carefully considered based on the competing usage and the regional situation into perspective.

Traditionally straw is collected in a semi-dry condition from the fields, getting bundled in slightly compacted bales to increase the handling and transportation logistics. Bales are formed using a baler densifying the chopped straw. Bales can vary in their sizes (L*B*D: 70-280 * 30-40 * 30-130; L*D: 120-150 * 60-180), shapes (cylindrical, square and rectangular) and density (120 to 180 kg m^{-3}) depending on the type of baler used (FNR, 2007; Clarke and Preto, 2011).

Further different densification processes are carried out on cereal straws to make their handling easier. The most promising densification process for straw is the press-agglomeration (press-pelletisation). Straw pellets are developing new markets in the agricultural sectors and are acting as an alternative to the traditional straw bales and simultaneously improving the logistics for the farmer.

2.4 Paper and pulp industries and their residual black liquor

In order to produce white paper, pulp is extracted from tree biomass, mainly consisting of celluloses and hemi-celluloses after separating lignin as process residue with the help of a chemical cooking processes in paper and pulp industries. Pulping industries mainly prefer coniferous / softwood biomass due to the presence of long celluloses fibres in comparison to that of hardwood biomass containing short celluloses fibres. The lignin content in coniferous biomass (28 – 41 %) is comparatively higher than that in the hardwoods (18 – 25 %) (Pastusiak, 2003; Schwarz, 2004; Hirth, 2009).

The utilization of coniferous biomass in the paper and pulp industry produces huge amounts of residues known as black liquors (50 Mio t a^{-1}) containing highly concentrated soluble lignin. Presently only 25 % of the lignin resource is exploited indicating the high availability and exploitation potential (up to 90 %) of this resource (Puls, 2009).

2.4.1 Chemical structure of lignin

Lignin is a hydrophobic, complex hetero-chain polymer and consists of three-dimensionally cross linked phenolic macromolecules building up with the combination of three basic monomeric building blocks, which are (i) p-coumaryl alcohol, (ii) coniferyl alcohol and (iii) sinapyl alcohol (Heitner et al., 2010) as shown in figure 3.

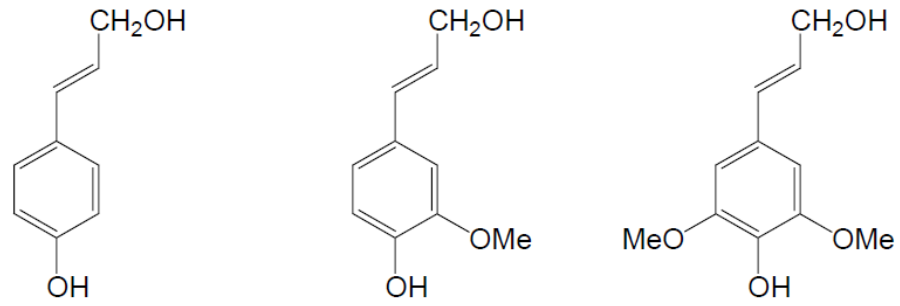


Figure 3: Lignin monomeric building blocks a) p-coumaryl alcohol, b) coniferyl alcohol and c) sinapyl alcohol (Heitner et al., 2010).

The monomeric building blocks are equipped with different functional groups (methoxyl, hydroxyl / phenol, aliphatic, aryl, alcohol and condense) as shown in figure 4. The principal monomer for softwood lignins is coniferyl alcohol, which has a methoxyl group (CH_30) on the C–3 position. Hardwood lignin's have two main monomers (coniferyl alcohol and sinapyl alcohol) having methoxyl groups (CH_30) on both the C–3 and C–5 positions. The third monomer, *p*-coumaryl alcohol, is more prominent in grasses and compression wood (branch conjunctures). The aromatic rings of the monomers are often referred to as (i) **guaiacyl** units having one aryl-OCH_3 group and are derived from coniferyl alcohol, (ii) **syringyl** units having two aryl-OCH_3 groups and are derived from sinapyl alcohol, and (iii) ***p*-hydroxyphenyl** units having no OCH_3 groups derived from *p*-coumaryl alcohol (Heitner et al., 2010).

Due to the presence of many phenolic groups, lignin is highly polarized which makes it react faster in both acidic and basic environments (liquid medium). Lignin mainly finds its application as adhesives / binders in many industries due to the high polarity of it influencing the binding potential (Benien, 2000; Pastusiak, 2003).

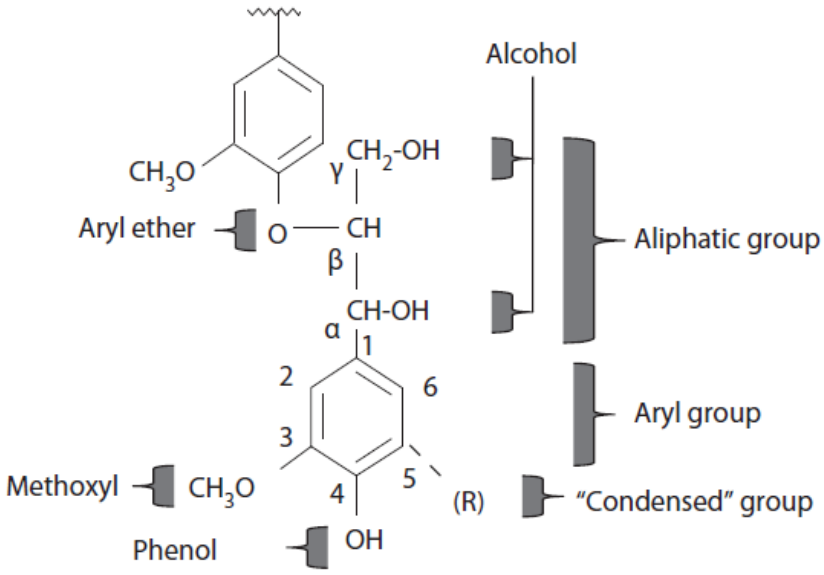


Figure 4: Lignin functional groups (Heitner et al., 2010).

2.4.2 Existing pulping processes

There are various pulp cooking processes for the separation of lignin and production of white pulp (celluloses and hemicelluloses) from wood. The most important chemical pulping processes are sulphite (acid) and sulphate (base) pulping, which are currently applied at industrial scale. Further there exist different alternative pulping processes such as i) hydrothermal - steam explosion, ii) organosolv, iii) polyol, iv) formacell-milox, v) monoethanolamin (MEA), vi) enzymatic (laccase, lignin-peroxidase), vii) nitric acid, viii) alkali sulphite anthrachinon methanol (ASAM) and ix) organocell, which can be also used in the production of cellulose and separation of lignin.

The isolated lignins are called technical lignin's as their structure and properties have been modified in the cooking process. The modifications depend on the various pulping process parameters (temperature, pressure, pH-value, time, etc.). This work concentrates mainly on the technical lignin's (sulphite and sulphate processes) produced at industrial scale.

2.4.2.1Sulphite and Sulphate pulping processes

The **sulphite pulping process** is the oldest method used for the production of pulp using acids in the pulping process. There are various methods of sulphite pulp production, currently the most dominant method is the acid bisulphite process using magnesium oxide (MgO) as base and sulphur dioxide (SO_2) in the form of bound and free SO_2 (free SO_2 in the form of H_2SO_3). Other methods utilize the calcium-bisulphite or the alkali sulphite process (Blechschmidt, 2010; Gruber, 2011).

The individual sulphite processing methods are dependent on the different parameters (temperature, pH value, strong acidic / strong basic, etc.) and are displayed in table 2.

Table 2: Different sulphite pulping parameters (Blechschmidt, 2010; Gruber, 2011).

Process	pH-range	Base	Active Reagent	Cooking		Yield (%)	Applications
				Temp(°C)	Time(min)		
Single-stage Sulphite pulping process							
Calcium-bisulphite	1-2	Ca^{2+}; Mg^{2+}; Na^{+}; NH_4^{+}	SO_2*H_2O; H^{+}; HSO_3^{-}	125-143	180-420	40-50	Pulp, Tissues, Chemicals
Magnesium-bisulphite	3-5	Mg^{2+}; Na^{+}; NH_4^{+}	H^{+}; HSO_3^{-}	150-170	60-180	50-65	Graphic papers
Neutral-Sulphite	5-7	Na^{+}; NH_4^{+}	SO_3^{2-}; HSO_3^{-}	160-180	25-180	75-90	Corrugated cardboard
AQ-Sulphite	9-13	Na^{+}	SO_3^{2-}	170-175	150-240	55-65	Similar to Kraft-pulp
Alkali-sulphite	9-13	Na^{+}	SO_3^{2-}; OH^{-}	160-180	180-300	45-60	Similar to Kraft-pulp
Double-stage Sulphite pulping process							
Stora 1	6-8	Na^{+}	SO_3^{2-}; HSO_3^{-}	135-145	126-360		
2	1-2		SO_2*H_2O; H^{+}; HSO_3^{-}	125-140	120-240	50-60	Greaseproof paper
Sivola 1	3-4	Na^{+}	H^{+}; HSO_3^{-}	140-150			
2	7-10		SO_3^{2-}	160-180	60-180	35-45	Chemical pulp

The active reagent in the acidic process is the hydrogen-sulphite ion (known as bisulphite ion (HSO_3^{-})), and sulphite ion (SO_3^{2-}) with different bases (calcium-oxide (CaO), sodium-oxide (NaO) or magnesium-oxide (MgO)). The basic chemicals promote the formation of phenolate-bonds (similar to that in sulphate pulping). Lignin undergoes a structural modification and becomes soluble in liquids due to the sulphonation reaction taking place in the sulphite pulp cooking process. The solubility of lignin is designated in achieving pure white celluloses and in easy removal of lignin from fibres.

The sulphonation is carried out mainly at the α-C atom of the ether unit (figure 5). The modification of a lignin molecule through sulphonation is a reversible process and can be reverse-modified with the help of a desulphonation process.

An extended sulphite pulp cooking process leads to the bond breakage of CH_2O groups and results in obtaining a better quality (improved lignin solubility) solution (figure 5b) with low molecular weight. The bond breaking of the CH_2O group plays an important role in making the lignin soluble (it is easily soluble at low molecular weights). The macro-molecule lignin is fragmented by breaking of α-O-4 and β-O-4 bonds.

The molecular weight of modified sulphite lignin ranges in between 1000 g mol^{-1} (delignification rate of 13 %) and 143000 g mol^{-1} (delignification rate of 92 %) after the cooking process (Grushnikov and Shorygina, 1971; Schwarz, 2004; Blechschmidt, 2010; Gruber, 2011) and is dependent on the delignification grade.

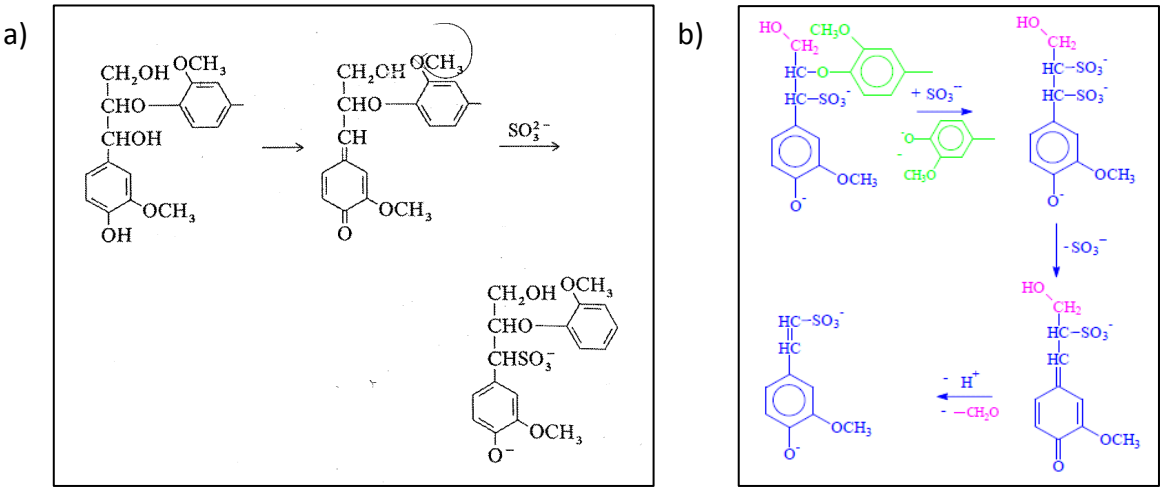


Figure 5: a) Breaking of lignin sulphonate through α-O-4 bond and b) sulphonation of CH_2O groups (Heitner et al., 2010; Blechschmidt, 2010; Gruber, 2011).

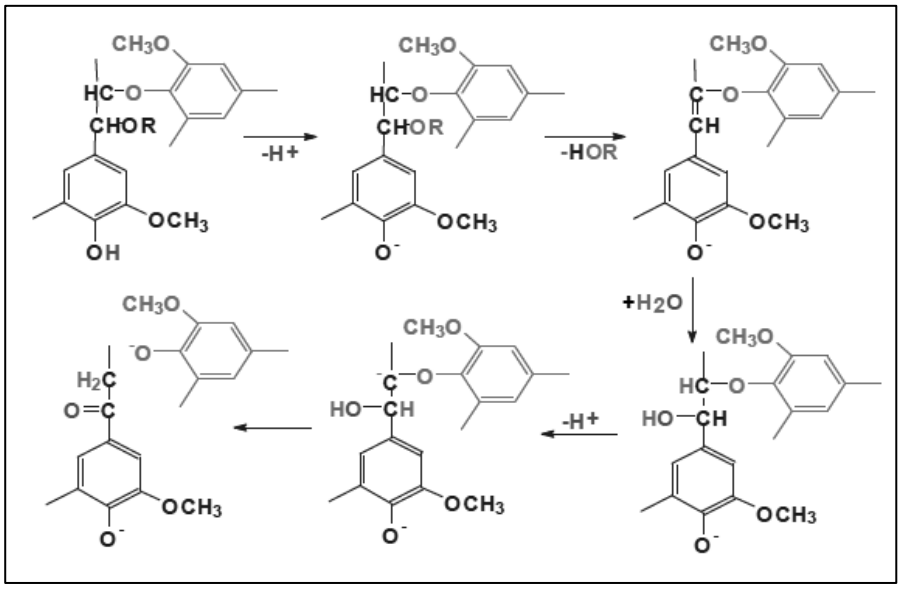
The **sulphate pulping process** can only be carried out in alkaline mediums with applied temperatures ranging between 160 °C and 180 °C for nine hours at a pressure of nine bar (Nitz, 2001; Müller, 2004). Sodium hydroxide (NaOH) and sodium sulphide (Na_2S) are used as pulping chemicals. The sulphate process receives its name through the addition of the make-up chemical sodium sulphate (Na_2SO_4) in the chemical recovery process. Sodium sulphide (Na_2S) hydrolyzes completely in to sodium hydro-sulphide (NaHS) in the cooking phase and becomes highly nucleophilic (electrons can be discharged easily). These nucleophilic sulphide-ions make the fission reactions to occur faster and more effectively in comparison to the pulp cooking process alone with NaOH.

The basis for the separation of cellulose and lignin with the help of the sulphate process is the soda process. The soda process was originally developed with sodium carbonate (Na_2CO_3) as the relevant base. Presently NaOH is used as a stronger base substituting Na_2CO_3.

The separation of lignin from celluloses in the sulphate pulping process can be explained in the following three chemical processes:

1. The phenolic groups of lignin are ionized and help in making the lignin soluble in liquids (figure 6a).
2. The second step is to break the ether bonds at the α-C-atom. The lignin molecule is separated with the nucleophilic substitution of the phenylpropane unit at the α-C-atom. It is also possible to separate the lignin at the β-C-atom of the ether bond.
3. The hydrogen atom on the β-C-atom can be separated in an alkaline environment. The resulting negative charge on the β-C-atom is shifted towards oxygen, through which a phenolate is formed and the connection to the residual lignin is broken (figure 6b) (Gruber, 2011).

a)



b)

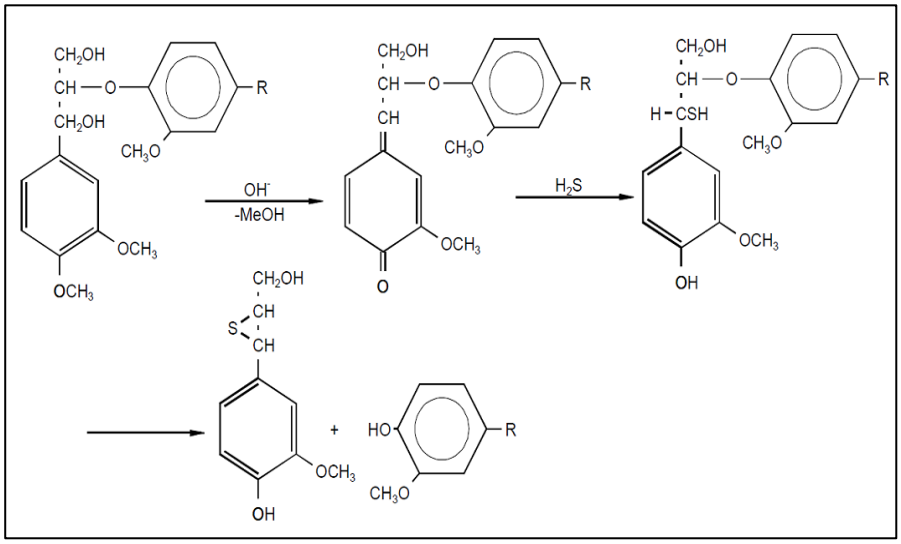


Figure 6: a) The three chemical proceedings in the delignification in soda-pulping and b) removal of lignin by breaking the β-C-atom bonds with the help of sulphur (Gruber, 2011).

The soda process disrupts predominantly the bond at the α-C-atom. The addition of sulphide-ion increases the effectiveness of the process by breaking also the β-C-atom bonds along with the α-C-atom bond (figure 6b). The effectiveness is dependent on the size of the sulphur atom and the presence of loosely bound electrons. This creates a so-called Thiran ring (3-chained sulphur-ring). This ring is very unstable and dissociates by building up of double-bond with the lignin molecule (Gruber, 2011).

The resulting lignin is known as Kraft lignin or alkaline-lignin and is bound with about 1-1.5 % of sulphur. Its molecular weight is about 2,000 to 3,000 g mol^{-1} and is only soluble in alkaline solutions / organic solvents (Semke, 2001). The yield of this process is about 40 – 50 % of the pulp and both softwood and hardwood biomass can be used.

The sulphate process also results in secondary and non desirable reactions such as the secession of methoxyl groups (-O-CH_3) to methyl-mercaptan (CH_3SH), dimethyl-sulphide (CH_3SCH_3) and dimethyl-disulphide (CH_3SSCH_3), which are highly toxic and smell intensely of hydrogen sulphide (H_2S). Further the nucleophilic separation is an ongoing reaction in both directions i.e. the progressive cooking results in partial re-linking of lignin fractions resulting in poor delignification grades. Thus the complete delignification with the sulphate pulping process is not possible. This is also the main reason for the darker colour of sulphate pulps compared to sulphite pulp and the requirement of increased bleaching (Blechschmidt, 2010; Gruber, 2011) in producing white paper.

2.4.2.2 Alternative pulping processes

In the last 20 years a lot of research has been conducted on **alternative pulping processes** with a specific focus on the reduction of environmental impacts and minimization of residues in comparison to the conventional industrial processes. These pulping processes use different chemicals, which are suitable to dissolve / selectively degrade lignin. Currently there are a variety of methods available and are listed below in table 3 and table 4. The different pulping processes are named based on the pulping chemicals used in their respective methods (table 3).

Several studies have shown that mixing of different pulping methods can lead to a better quality of the pulp and increase the yield and flexibility of the product. Advantages of two or more combined methods (hybrid methods) can be utilized by combining different methods together, which simultaneously minimize the disadvantages in comparison to the single methods (table 4).

Table 3: Different alternative pulping methods, their names and the chemicals used.

Method	Chemicals
Organosolv method	Organic solvents such as methanol (CH_3OH), ethanol (C_2H_5OH), propane
FORMA-CELL, MILOX method	Organic acids such as formic acid, acetic acid, peroxy acid
MEA Process	Monoethanolamine
Enzymatic digestion	Laccase, lignin peroxidase
Nitric Acid	Nitric acid (HNO_3), ammonia (NH_3)

Table 4: Hybrid pulping methods.

Method	Chemicals
ASAM (Alkali-Sulphite-Anthraquinone-Methanol) process	Combines the modern catalyzed Sulphite pulping process with the Organosolv process
Organocell process	Combines the Soda-Anthraquinone pulping with the Organosolv process

2.4.3 Methods to separate lignin from black liquors

Black liquors produced in the industrial processes come with 20 % solid matter contents and are generally evaporated to increase the solid matter contents up to 30 % (Miletzky, 1985; Panda, 2002). The liquors with increased solid matter contents are then treated with acids (Panda, 2002) to separate the lignin from black liquors. **Acidification** is the process of treating raw and residue materials with different acids and their mixtures. Acidification of black liquors is a highly tedious process involving a number of consecutive process steps. Acidification is conducted first by reducing the pH-value of black liquor (sulphate black liquor) from pH 12 to pH 9 using carbon dioxide (CO_2) gas. This precipitates about 60 to 70 % of the lignin as sodium-lignate salt. This salt is either heated such that it coagulates and makes the filtration process easier (Panda, 2002) or it is further treated with sulphuric acid (H_2SO_4) (Ohman et al., 2006; Ohman et al., 2010). The lignin obtained is then purified by suspending and washing it in water, which reduces the pH value of the lignin to 3 or less. The resulting liquor from this water washing process is sent back to a recovery system and mixed together with the raw black liquor after evaporation. Acidification of black liquor is only advisable to carry out with CO_2 and H_2SO_4 as the resulting liquor from the precipitation process has to return back to the raw black liquor.

The **LignoBoost process** (figure 7) provides a method for separation of lignin from black liquor using an acidification process (Ohman et al., 2006; Ohman et al., 2010; Tomani, 2010) and comprises of the following process steps:

1. Precipitating the lignin by acidification with CO_2 and thereupon dewatering through filtration with the help of chamber press filters (filter 1),
2. Suspending the obtained lignin and adjusting the pH-value equal to that of washing water by acidification (re-slurry),
3. Dewatering of the suspension from step 2 through filtration,
4. The obtained lignin is washed with water by performing a displacement washing without any significant changes in the pH-value, as the changes in the pH-value affect the ionic strength and the solubility properties of lignin in the slurry and
5. Dewatering the lignin from step 4 through filtration with the help of chamber press filters (filter 2).

The filtrate from filter 1 is sent back to the strong black liquor evaporation equipment (30 % solid matter content) to keep the concentration of lignin constant throughout the operation. The filtrate from filter 2 is sent back into the weak black liquor evaporator (20 % solid matter content).

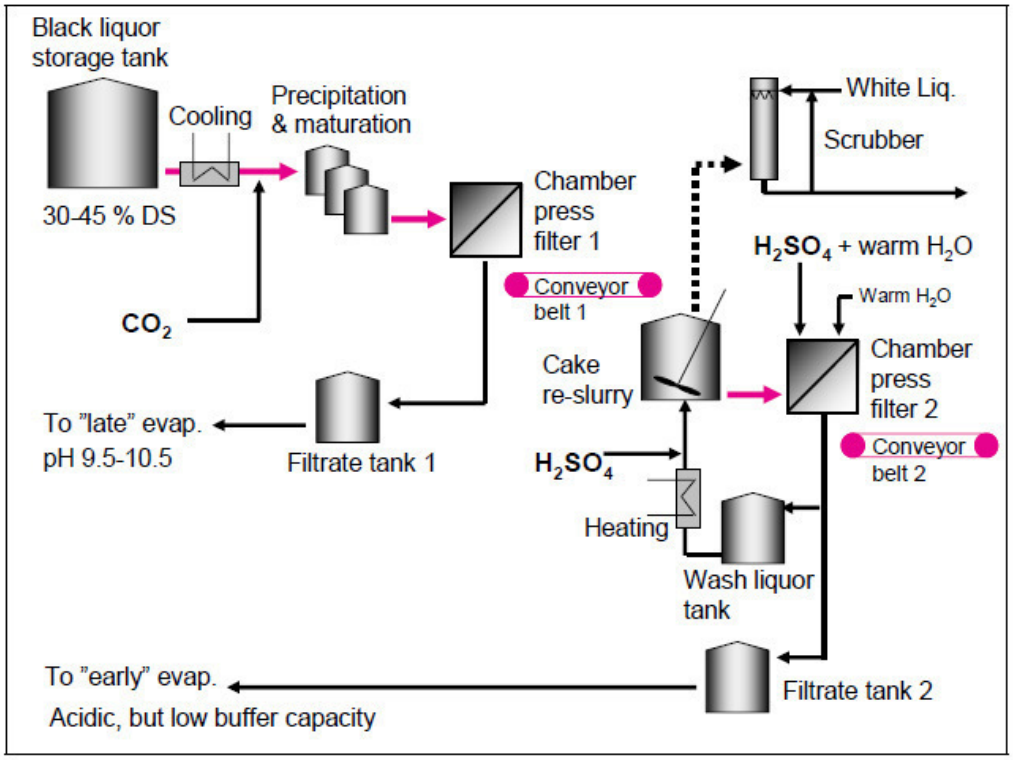


Figure 7: Schematic layout of the LignoBoost process precipitating lignin using consecutive acidification and washing processes (Tomani, 2010).

2.5 Biotechnological (fermentation) process and its residues

Fermentation is one of most dominant biotechnological process used for extracting energy by the oxidation of organic compounds such as carbohydrates. Materials with high concentrations of sugars / carbohydrates are the most commonly used substrates for the fermentation process. The main products of the fermentation process are methane, ethanol, lactic acid, lactose and hydrogen, where as the by-product is the fermentation residue.

Biogas (bio-methane) is produced from biomass using fermentation (wet or dry fermentation) as the main process step. Bio-methane is the methane gas (CH_4) generated from biogenous raw and residue materials with the help of biotechnological conversion processes (bio-chemical, thermo-chemical). The main components of a biogas plant (figure 8) are the i) conditioner, ii) fermentor, iii) gas storage and iv) combined heat and power (CHP) plant.

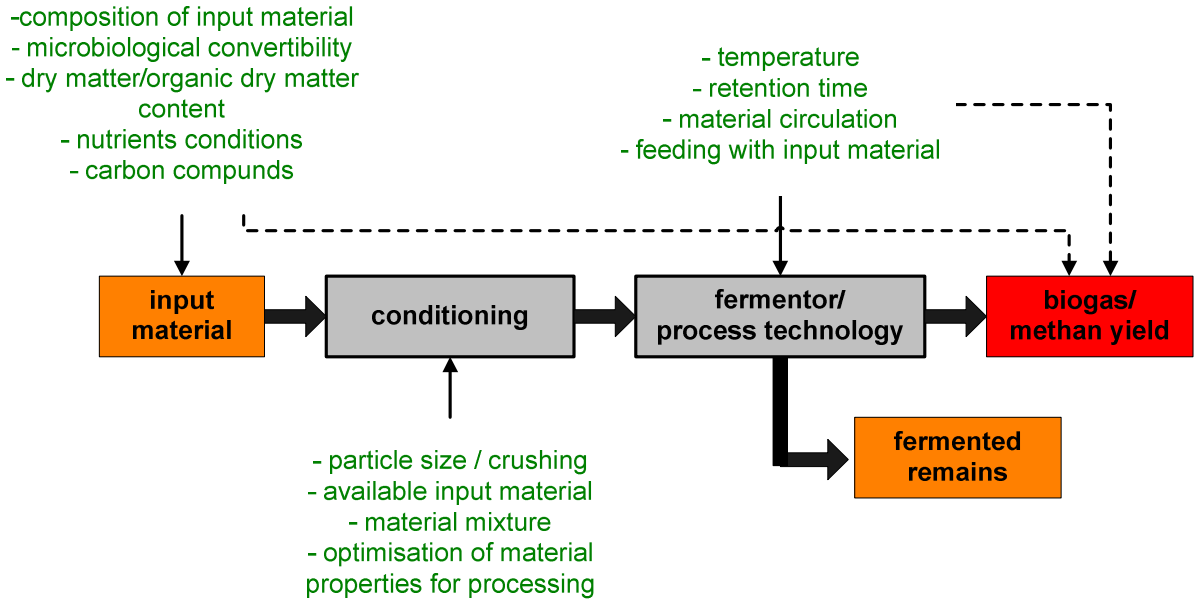


Figure 8: Schematic process pattern of biogas plants with their individual influencing parameters.

Biogas mainly consists of 50 – 65 % methane (CH_4), 35 – 50 % of carbon dioxide (CO_2) and traces of hydrogen sulphide (H_2S), ammonium (NH_4-N), hydrogen (H_2) and carbon monoxide (CO). The produced biogas is then cleaned and fed into a combined heat and power (CHP) facility, where it is converted into heat and electricity.

The different raw and residue materials are prepared in a mixing tank by mixing the specific blend mixtures together to form a relatively homogeneous mixed mass as substrate for fermentation process.

The anaerobic digestion of this homogenous blend mixture is carried out in the main fermentor at different temperature conditions (psychrophil up to 20 °C, mesophil in between 35 °C and 40 °C, thermophil in between 50 °C and 60 °C) depending on the material characteristics and the chosen fermentation process (wet or dry).

The metabolic activities of the microorganisms degrade the substrate mixture in the fermentor producing biogas and the residues are known as fermentation residues (NEP, 2012).

The **fermentation residue** characteristics are mainly influenced by the i) input materials and their blend mixtures, ii) type of fermentation process and on the iii) process parameters. These dissimilarities lead to characteristic differences (dry matter content, size and shape of fibres, etc.) of the fermentation residues. The fermentation residues generally have a lower pH value and are enriched with nitrogen (ammonium) and potassium concentrations in both the solid and liquid phases (Bayerische Landesanstalt für Landwirtschaft, 2009). These factors make the fermentation residues suitable for their utilization as fertilizer.

The composition of input materials from animal husbandry before fermentation process have a dry matter content of about six to eight percentage (6 – 8 %) with an average total nitrogen content of 3.6 – 3.8 kg t^{-1} (1.6 – 2.5 kg t^{-1} ammonium nitrogen (NH_4-N), 0.6 - 0.7 kg t^{-1} of phosphorus, 2.1 - 2.8 kg t^{-1} of potassium and 0.6 kg t^{-1} of magnesium) (Landeskontrollverband Brandenburg e.V., 2012; Thüringer Landesanstalt für Landwirtschaft, 2005). Whereas the input materials from agricultural sectors (plant residues) have a dry matter content of about 32 % with a total nitrogen content of 1.2 % (11.3% of NH_4-N, 0.24 % of phosphate and 1.13 % of potassium) (Thüringer Landesanstalt für Landwirtschaft, 2005; Vogt et al., 2008).

The materials after the anaerobic fermentation process from both animal husbandry and agricultural sectors display altered compositions in both liquid and solid phases due to the conversion of solids to methane in the process. The dry matter content with respect to cattle manure is around 3.8 % to 5.8 % and for plant residues is about 10.6 %. The fermentation residues denote an increased concentration of total nitrogen from 3.6 to 10.7 kg t^{-1} along with increases in ammonium content from 1.6 to 8.3 kg t^{-1}, phosphorous content from 0.6 to 6.9 kg t^{-1} and potassium content from 2.1 to 12.6 kg t^{-1} (Thüringer Landesanstalt für Landwirtschaft, 2005; Vogt et al., 2008; Jacobs, 2010).

The different distributions / compositions of nutrients in the liquid and solid phases clearly display that the fermentation residues are suitable for their direct usage as liquid fertilizers. The efficient use of fertilizers can only be achieved when both liquid and solid phases are utilized together with specific refinement of the conventionally applied processes.

Conventionally, to solve the storage and handling problems of the residues, the solid residues are densified after separating the liquids from the solid-liquid substrate mixtures. The liquid separation process and pelletisation of the solid residues reduce the fertilizer efficiency of the solid residue pellets by around 46 % of total nitrogen with about 53 % reduction of ammonium, 32 % reduction of phosphorous and 52 % reduction of potassium contents, which are mainly concentrated in the liquid phase (table 5). Table 5 also shows that the solid phase material after solid liquid separation contain about 75 wt. % liquid contents, indicating only a marginal reduction of liquid contents of about 10 wt. % to 23 wt. % (from 97 wt. % to 75 wt. %). This high liquid content in the solid phase is due to the inefficient mechanical separation processes making the process highly tedious. The thermal solid-liquid separation though evaporation process is not advisable due to high amount of energy requirement and also results in high N_2O emissions. The high N_2O emissions are due to the evaporation on ammonium nitrogen above 50 °C temperature.

The fermentation residues after separation into solid and liquid phases are analyzed for their individual phase concentrations of nitrogen, phosphorous and potassium contents (Bayerische Landesanstalt für Landwirtschaft, 2009), which are given in table 5 along with the minimum and maximum values (depending on substrate mixtures) combined within both the liquid and solid phases together.

Table 5: Analysis of the fermentation residues with combined (both solid and liquid) phases and as individual phases (Bayerische Landesanstalt für Landwirtschaft, 2009).

Fermentation Residues		Dry Substance (wt. %)	Total Nitrogen (Kg m^{-3})	Ammonium NH_4 (Kg m^{-3})	Phosphorous P_2O_5 (Kg m^{-3})	Potassium K_2O (Kg m^{-3})
Combined phases	Min.	2.9	2.4	1.5	0.9	2.0
	Max.	13.2	9.1	6.8	6.0	10.6
	Mean	6.7	5.4	3.5	2.5	5.4
After solid-liquid separation in individual phases						
Liquid-Phase (Mean)		5.7	4.9	3.0	2.3	6.2
Solid-Phase (Mean)		24.3	5.8	2.7	5.0	5.8

Further the conventional separation process not only reduces the fertilizer efficiency, but also creates problems with groundwater and water-bodies contamination as the directly sprinkled liquid percolates / drains / seeps faster in the field than dry fertilizers. This fast seepage of the liquid phase also results in a reduction of the nutrients availability to plants reducing the overall fertilization efficiency (open plant nutrient cycle).

2.6 Particle size distribution

Particle size analysis is the measurement of particle sizes and shapes. The material being subject to particle size analysis has a dispersed form containing particles of different sizes and shapes. Particle size analysis serves the purposes of obtaining information on the exact numerical amount, size and shape of the particles of the dispersed material (Bernhardt, 1994).

The particle size is defined by one geometrical parameter, which could be the length or width, area or volume of a particle. The choice of parameters varies according to the measurement system used, as different measurement systems use different physical particle characteristics.

The physical particle properties, which could be obtained from the granulometric characteristics of particle sizes are either through the measurement of mass or sedimentation rate or field disturbance effects of the particle (Bernhardt, 1994).

Particles can be classified according to their size into

- Colloid-disperse or ultra-fine particles with a size range between 1 nm and 1 µm,
- Fine-particles (dust) with a size range between 1µm and 100 µm and
- Coarse-particles with a size range from 100 µm into a size range including centimeter (cm) sizes (Stark, 2003).

Further Pruden, (2005) classifies the fibrous particles into long fibres, short fibres, slime stuff (Schleimstoff) and flour stuff as shown in figure 9. This classification is given based on the fibres obtained from paper and pulp industries.

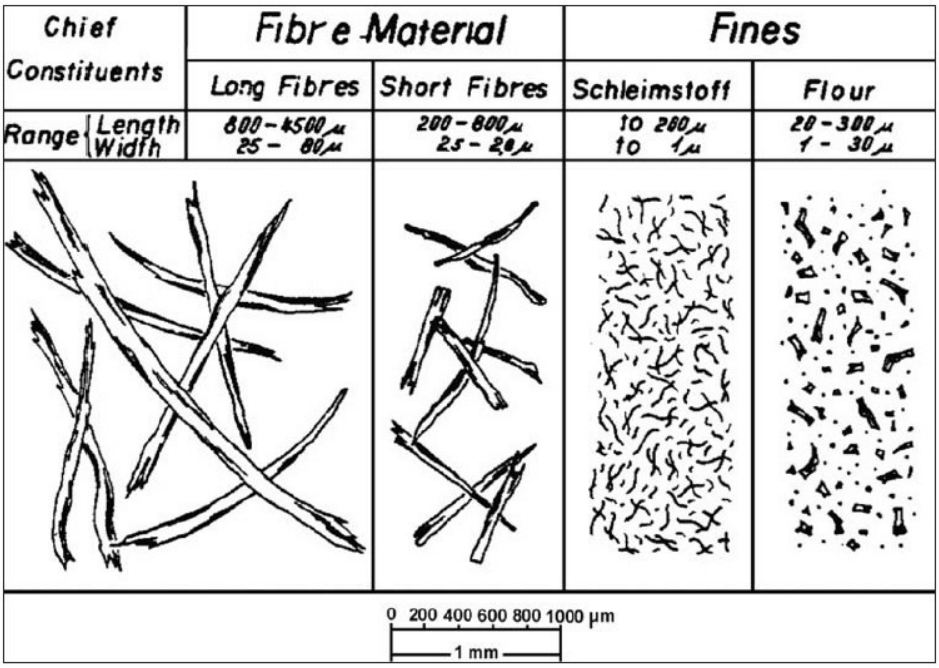


Figure 9: Classification of fibres (long fibres and short fibres) and fines (slime stuff and flour) as per Pruden, (2005).

2.6.1 Sieve analysis

The determination of particle size and particle shape can be carried out using different techniques. The oldest, most common way of determining particle size is the **sieve analysis**. The main advantages of sieving are the analyzing relatively large sample amounts with comparatively small work effort. The analysis uses a simple technical and controllable use of the system (Paulrud, 2004).

The principal of sieving is that a known mass of sample material is placed on a tower of vibrating sieves with downsized aperture sizes from top to bottom with a pan below. The vibrating sieves distribute the sample material into different size classes. The size distribution is measured gravimetrically by noting down the sample materials mass retaining on the corresponding sieve (Bernhardt, 1994).

The passage of particles through a sieve depends on the shape of the particles, the shape of the sieves aperture and on the orientation of the particles with respect to sieves apertures. A characterization of particle shape is not possible within sieve analysis (Bernhardt, 1994; Grover & Mishra, 1996; Paulrud, 2004).

2.6.2 Image analysis

Another method of particle size analysis is the **image analysis**. For quality control not only the particle size is of importance, but also the particle shape is an important characteristic. The complete dimensions of single particles can be analyzed with the help of image analysis. Within image analysis, different size characteristics (particle length, particle width, particle area, etc.) for each particle are measured and the shape characteristics are calculated thereof. During image analysis, images of the particles are obtained in several ways, depending on the image analysis systems.

Stieß (2009) states that certain requirements on images or pictures of particle collectives for analysis on particle number, size and shape are crucial. The pictures need to feature an acceptable big amount of particles, as every size class needs to be represented in its relating numbers in the picture. Furthermore single particles have to be projected separately, i.e. the particles have to be optically separated from each other for a better optical differentiation. Another aspect which has to be considered is the contrast of the pictures for a better perceptibility of the outline of particles.

Different methods of optical image recognition exist. The particles are fixed on a glass carrier in the static picture analysis (microscope). The static picture analysis is tedious, especially when the sample contains a combination of fine fibres and fine dust particles together. The dynamic picture particle size analysis (snapshots of moving particles in an air / liquid channel will be evaluated) is comparatively faster and can measure higher number of particles in a given time period.

2.6.3 Laser diffraction method

The third method of particle size analysis is the laser diffraction. In laser diffraction, the particles are made to pass through a laser beam in the laser diffraction and are either located in an air stream or dispersed in a fluid medium. The light from the laser beam is scattered when the light hits the particles at an angle that is inversely proportional to the particles size. By applying the light scattering theories of Mie and Fraunhofer to the angular intensity of the scattered light, it is possible to calculate the particle size (Paulrud, 2004).

Particle concentrations for the use of laser diffraction for particle size analysis need to be very small, so that particles are not situated too close together and thus cannot be recognized as one big particle. Laser diffraction is usually used for the particle size analysis of very small particles, ranging from a size of 0.02 to 2000 µm (Stieß, 2009).

2.7 Agglomeration

Agglomerates are formed as a result of particles accumulation in the agglomeration process and the produced agglomerates can vary in their sizes. The produced agglomerates are given different names based on their sizes (granules < 3 mm; 3.15 mm < pellets > 25 mm; Briquettes > 25 mm in diameter), shapes (spherical, cylindrical, rectangular, etc.) and the application of different processes. The main agglomeration processes are (i) flocculation and coagulation (bulk accumulation of particles in liquid phase), (ii) build-up agglomeration (moist-granulation, pelletisation, coating of dragees, etc.), (iii) press agglomeration or densification (compaction, briquetting, tablets, etc.) and (iv) melt agglomeration (sintering).

Agglomeration processes produce agglomerates having uniform size and shape and their choice of application in many industries is based on the required end product characteristics.

Flocculation and coagulation are the aiding processes used in separating the suspended solids (mostly colloidal size) with the help of flocculants and coagulants (generally used in waste-water treatments). The flocculants and coagulants bring the fine colloidal particles together and develop into an agglomerate and sediment (figure 10) due to their increased weights.

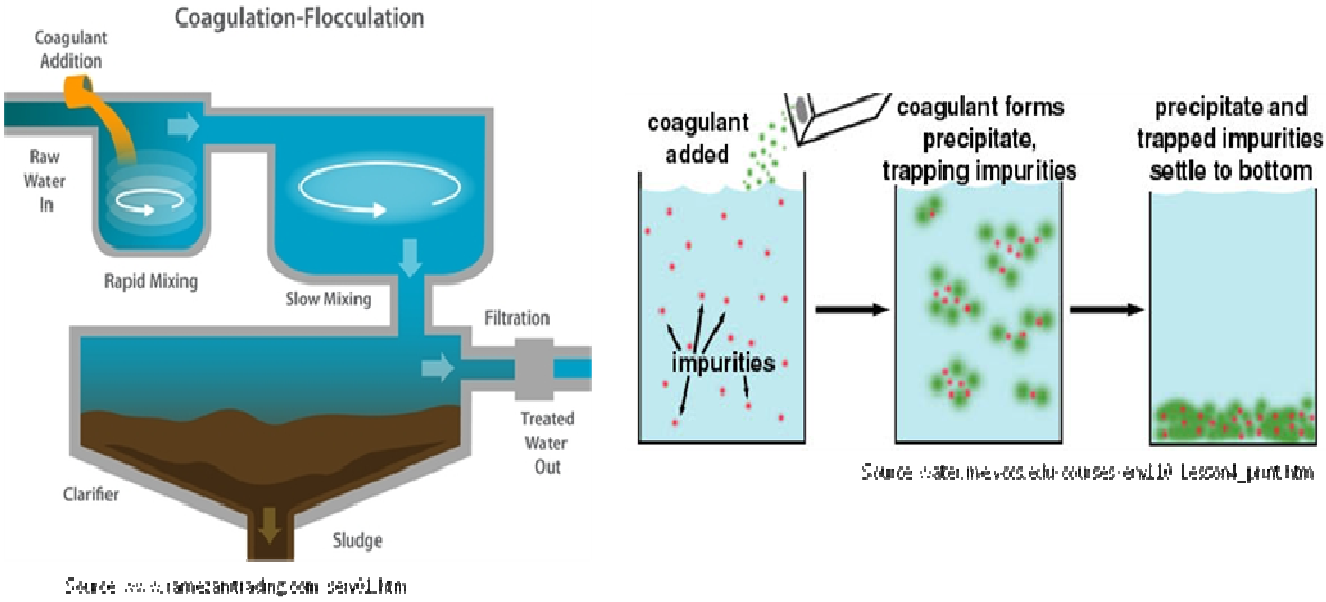


Figure 10: Flocculation and coagulation are the aiding processes used in separating the suspended solids (water.me.vccs.edu, www.ramezanitrading.com, last visited on 15.7.2012).

The **build-up agglomeration** is a process of moist / wet granulation carried out with the help of either pelleting discs or pelleting mixers or spray-granulation. The loose particles develop into agglomerates due to capillary bonding forces. Build-up agglomeration is used where the end products have to be bound loosely having spherical shape (figure 11).

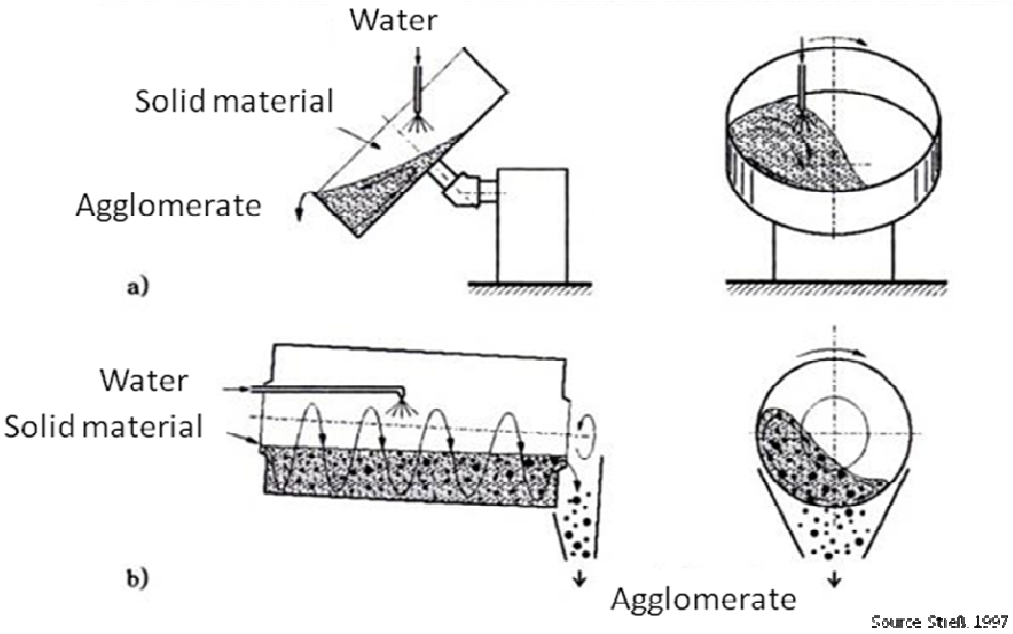


Figure 11: Build-up agglomeration process using pelleting discs or pelleting mixers (Stieß, 1997).

The **press agglomeration** is a process of densification of dry matter with high pressures and is applied where the end products are desired with high densities. The agglomerates produced with the press agglomeration process are generally noted as pellets or briquettes (figure 12).

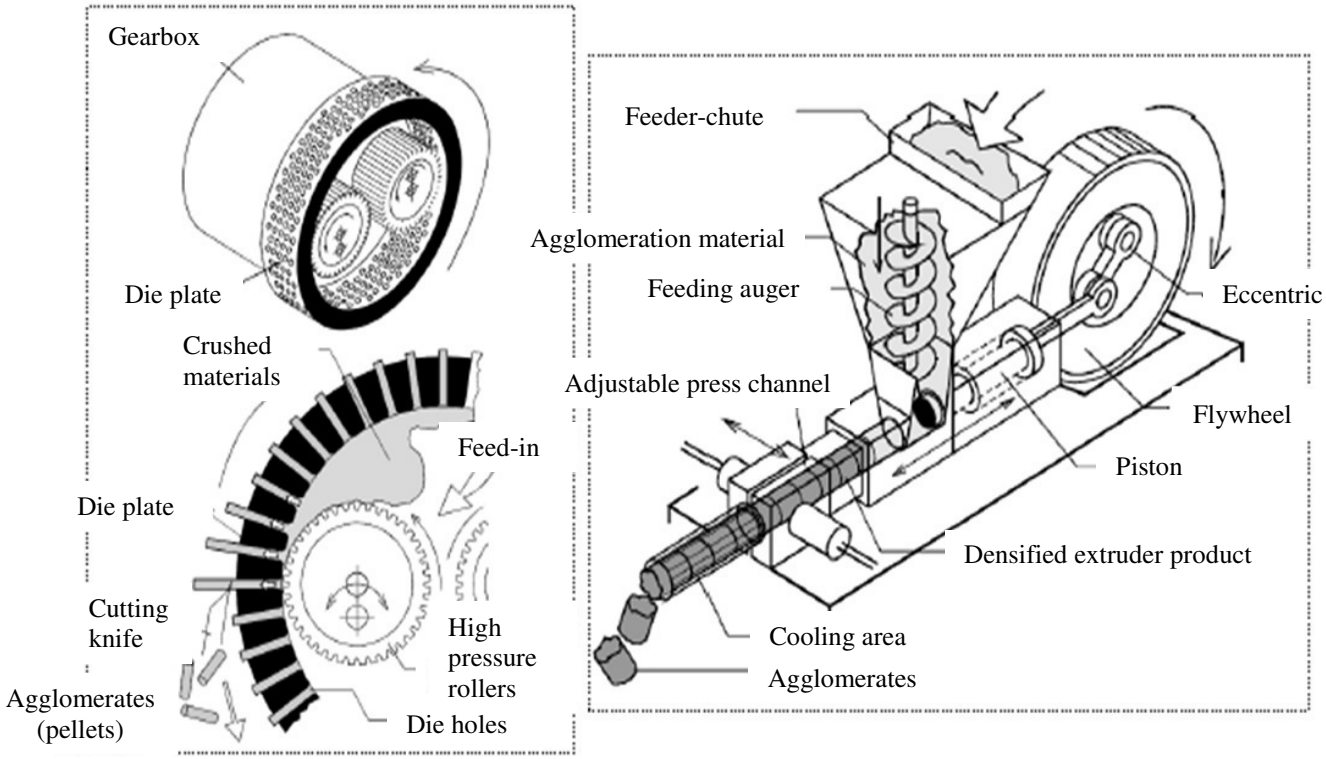


Figure 12: Press agglomeration process for pellets using roller moulds / dies and for briquettes using piston extruder (Hartmann, 2001b).

Melt / sinter agglomeration is a process of supplying heat to material, through which the primary particles melt and develop into agglomerates (granules / pellets / briquettes) and gain stability during the cooling of particles. Melt agglomeration is applied mostly in metals and plastics processing industries. Melt agglomeration can be carried out either through coalescence or immersion based on the required end-product (figure 13).

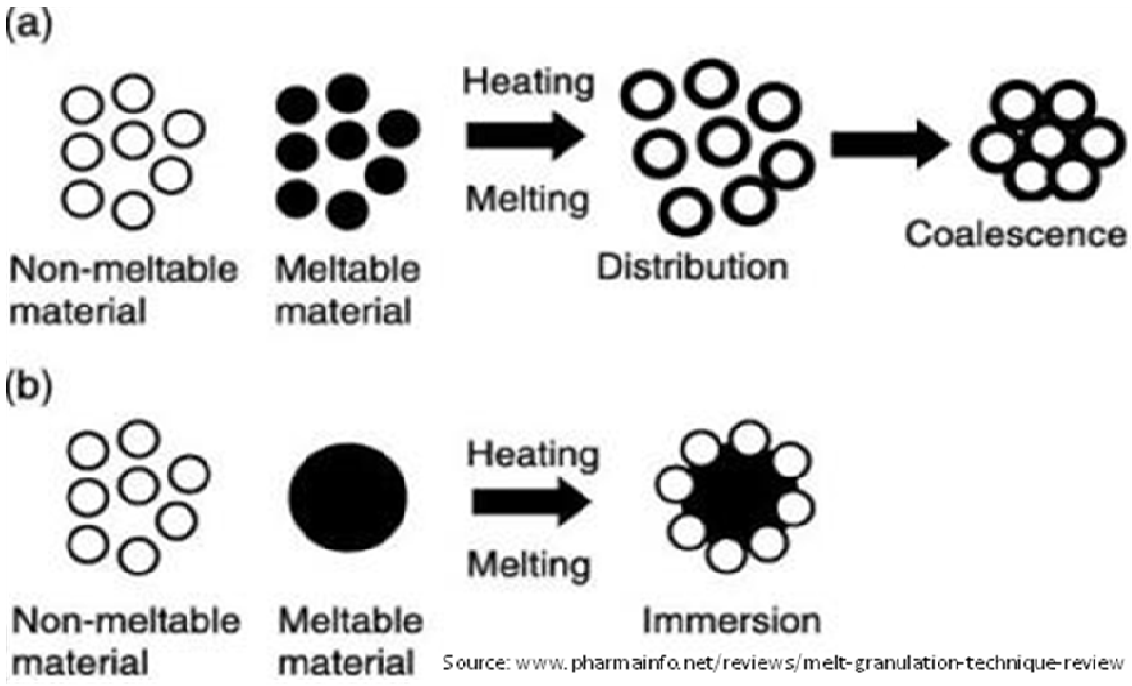


Figure 13: Coalescence and immersion melt-agglomeration process in metals and plastics processing industries (www.pharmainfo.net, last visited on 15.7.2012).

2.8 Influence of water (moisture) content on the heating value of material and in the agglomeration process

The water content or moisture content (w) is generally obtained from the fresh biogenous materials and describes the amount of water or moisture present in them. The water or moisture content is obtained by drying the fresh biogenous materials and measuring the differences in weight loss due to evaporation of water.

The water content of the fuels is obtained from the dry fuel materials unlike for the raw materials (fresh matter) and is defined as the ratio of fuel bound water to the dry mass of the fuel (FNR, 2007).

Water content is the most influencing parameter, which determines the heating values of the materials or fuels. Since biomass in nature comes with high water contents, this high water contents has to be evaporated in the combustion process. The evaporation energy required reduces the net energy yield due to reduced released energy (FNR, 2007). The influence of water content on the heating value can be determined using equation 1.

$$H_{u(w)} = \frac{H_{u(wf)} \cdot (100 - w) - 2{,}44\ w}{100} \qquad (1)$$

H_u (w) is the heating value (MJ kg^{-1}) of the fuel containing bound water (w). H_u (wf) is the heating value of fuel dry matter. The constant 2.44 in equation 1 is the heat of evaporation of water in MJ kg^{-1} at 25 °C temperature (FNR, 2007). Figure 14 displays the relationship between the water content and the heating value of the fuel. A linear decrease in the heating values of the wood biomass fuels was observed with increasing water contents calculated as per equation 1 (FNR, 2007). The average heating value of wood is 18.5 MJ kg^{-1} with zero percentage water content and zero percentage fuel bound water content, which linearly reduces to zero MJ kg^{-1} heating value at approximately 88 wt. % of water content and approximately at 730 wt. % of fuel bound water content.

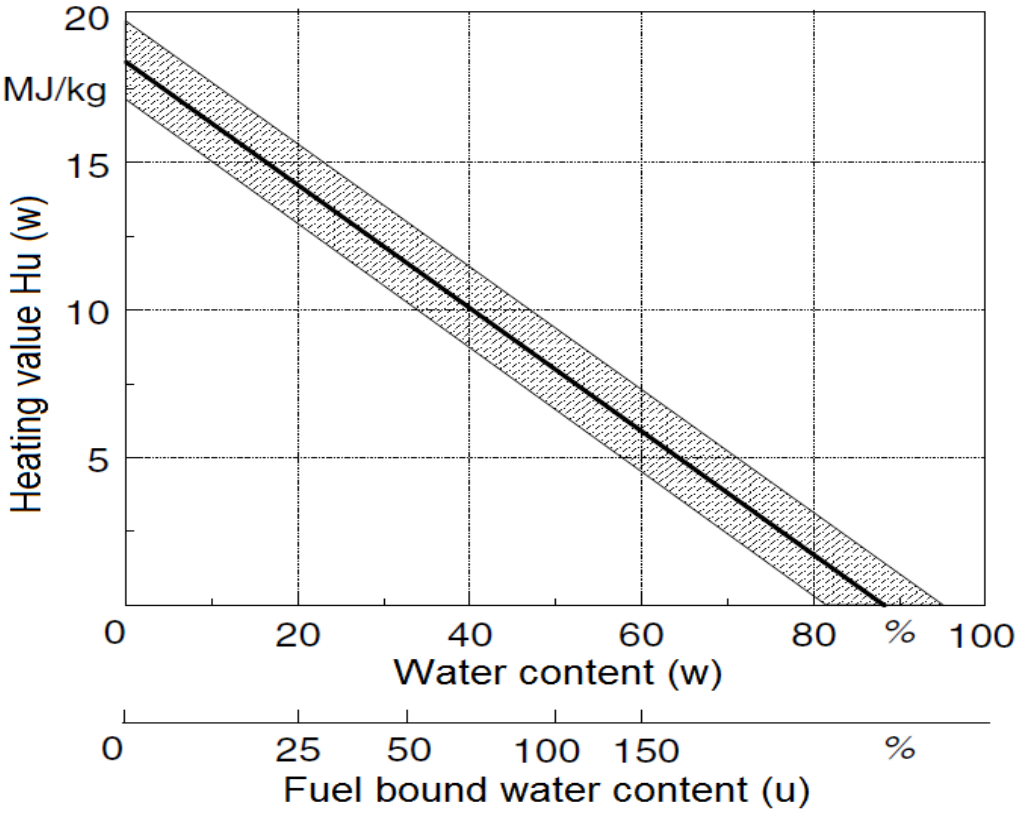


Figure 14: Influence of water content on the heating values of fuel with wood as example (Nussbaumer and Kaltschmitt, 2001; FNR, 2007).

The required water content for the pelletisation process is mainly dependent on the applied pelletisation process and on the characteristics of the raw materials. The raw materials with high water content have to be dried or dewatered before pelletisation (Salzbrenner and Preuß, 2007). The press-pelletisation process with low water content is not possible due to the high frictional forces occurring in the mould or die channels. It is advisable to carry out pelletisation of biomass with a minimum water content of at least 8 wt. % (Obernberger and Thek, 2009).

The water content also plays an important role in the wet build-up pelletisation process of materials by acting as bridging and binding material. The binding potential of the water is dependent on the grade of saturation (S) and capillary pressures (P_k) as shown in figure 15 (Stieß, 1994). The liquid binding potential is defined as the volume percentage of liquid present in the agglomerate cavity.

The transmission of adhesive forces at the liquid and raw material contact point takes place in the liquid bridging region. The grade of saturation in this region is below 25 %. Capillary pressures occur between the particles when the cavities are completely filled with liquids. The grade of saturation in this region is higher than 80 %. Between the bridging region and capillary pressure region is the transitional region. This region contains liquid bridges as well as the saturated regions inside the agglomerates (Stieß, 1994; Schubert, 2003).

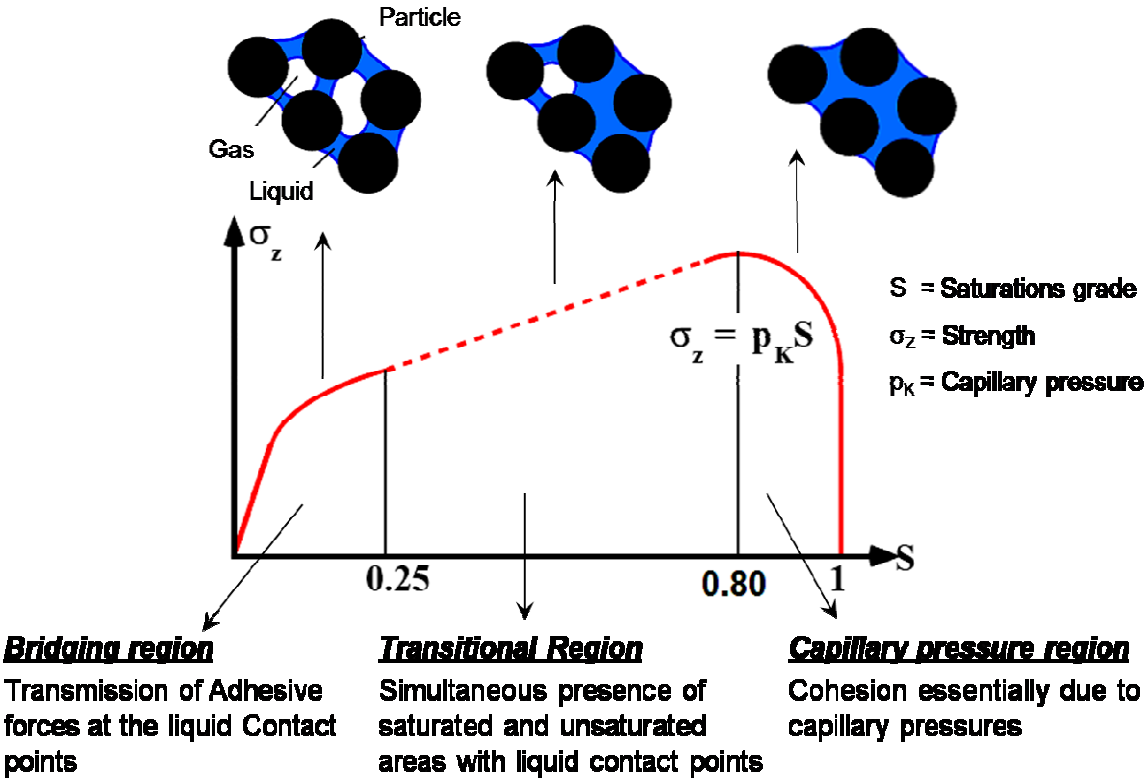


Figure 15: Capillary pressures (p_k) und tensile strength (σ_z) of produced wet agglomerates or pellets with respect to the grade of saturation (S) and their different regions (bridging, transitional and capillary pressure regions) (Stieß, 1994; Schubert, 2003).

2.9 Biomass Pellets

Fibrous biomass pellets (ex. sawdust, straw, etc.) are agglomerates, which are produced using press agglomeration with moderate or high densification pressures. Various factors (raw material, water content, degree of comminution / grinding and type of the die, etc.) influence the pelleting process and their quality or throughput. The grinding and water content of the materials are the most important parameters in the pelleting process. Further the process is also influenced by the addition of binders / additives. The addition of binders / additives is specific to the required end-product quality characteristic.

The interaction of different size fractions in coarsely dispersed systems play an important role in many processes, especially with the fine particles. The fine particles influence or control the binding forces in the pelletisation process. The main binding force acting on the adjacent particles or groups of particles as well as between the particles and dispersing agent is the VAN-DER-WAALS force. In addition the bonding of particles is also influenced by applied mechanical forces, capillary forces, adhesion force, interlocking of particles, etc.

The adhesion force depends on the number of interacting surface contact points between the particles. The contacts between the particles in the press agglomeration are improved with the help of densification pressures applied against each other.

2.9.1 Biomass pellet market and standards

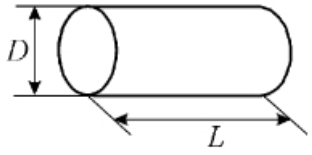
The pellet market in Europe demands high quality standardized products due to the fact that the majority of the pellets will be used in small scale facility boilers for heat and electricity generation.

The various standards specifying the pellet quality are mainly based on physical properties (size, shape, density, abrasion / durability, etc.), chemical substances present (water content, chemical composition, heavy metals presences, etc.), security issues, ease in handling (low dust), boiler specifications (small: < 15 kW, medium: 15 - 100 kW, large: > 100 kW) and low toxicity in production and utilization of biomass pellets.

The standards DIN 51731, DINplus and Ö NORM are the most commonly referenced standards for biomass pellets prepared in Germany and Austria. The new European standard EN 14691 further substantiates the biomass pellets based on their end quality into different grades (grade: A, B and C). The detailed standards specified in the norms are given in table 1 (chapter 1).

2.9.2 Shape and Size

Biomass press pellets are classified to be cylindrical in shape according to the current European standard EN 14961. The classification is further distributed / divided into five different size classes having diameters ranging from 6 mm to 25 mm and lengths ranging from 3.15 mm to 50 mm (figure 16).



L Length
D Diameter

Diameter (D) and Length (L)	
$D06$	6 mm ± 1,0 mm and $3{,}15 \leq L \leq 40$ mm
$D08$	8 mm ± 1,0 mm and $3{,}15 \leq L \leq 40$ mm
$D10$	10 mm ± 1,0 mm and $3{,}15 \leq L \leq 40$ mm
$D12$	12 mm ± 1,0 mm and $3{,}15 \leq L \leq 50$ mm
$D25$	25 mm ± 1,0 mm and $10 \leq L \leq 50$ mm

Figure 16: Shape and size of biomass press pellets as per the standard EN 14961.

2.9.3 Density

The density of pellets (bulk density, pellet density) is an important property as it improves the storage, transportation and handling efficiencies. The bulk density of pellets is calculated by measuring the bulk weight of the pellets filling a pre-defined volume, whereas the pellet density is calculated by evaluating the average of the measured volume and weight of single pellets.

2.9.4 Constitution / layout of biomass press pellets

The produced biomass press pellets displays a pronounced / layered disc-like fibre structure with broken ends (figure 17). The pronounced / layered disc-like structure is due to the compression / densification forces acting on the fibre particles in a mould / die (Holm et al., 2006). The disruption generally occurs at the transition points between the layers, indicating the influence of strength / durability on the build-up of press pellets.

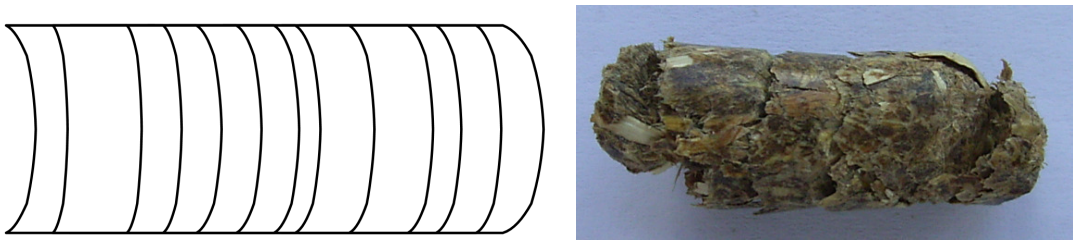


Figure 17: Schematic layout / build-up of particles in biomass press pellets (Holm et al., 2006) and the produced biomass (straw) press pellet.

2.9.5 Abrasion and Strength

Abrasion / durability and strength (diametrical, point and 3-point) of pellets are considered as the most important mechanical parameters in their quality assurance and are standardized under DIN CEN / TS 15639. Abrasion and strength are the measurement of pellets resistances against the application of various forces. Both abrasion and strength tests result in the size reduction / disruption (dust development) of the pellets in one or the other form due to different forces acting on the pellets. This disruption causes inconvenience to the end-user due to development of dust. The disruption / deformation of the pellets take place with application of external forces in various processes (transportation, storage, feeding systems, etc). The disruption stresses can be elastic (reversible), plastic (irreversible) or viscous (deformation rate dependent on temperature) in their behavior.

Disruption generally initiates at the point of non-homogeneity and extends further depending on temperature and rate of applied load. The influence of disruption stresses on the pellets / particles can be related to the intensity and rate of the stress applied. The intensity and rate of the stress result in different disruption characteristics (Schubert, 1989) of the particles (figure 18).

Stieß, (1997) states that strength is the measure of resistance against applied external forces / stresses (impact, bending, shear, abrasion, etc.) and is influenced by physico-mechanical properties (shape, size, porosity, density, etc.) of the pellets. The physico-mechanical properties interact with each other and are strongly influenced by binders, additives, water content etc (Kaltschmitt et al., 2009; Obernberger and Thek, 2009). Pellets should therefore have to possess necessary strength to facilitate the easy handling characteristics.

The measurements of stress resistance of pellets / agglomerates can be carried out using different test methods. These test methods are generally applied on agglomerates in different industries (pharmacy, metalworking, plastics, etc.) and are used in specifying the quality standard of the products. Single particle test measurements are applied for agglomerates > 5 mm (Stieß, 1997). The conventional tests check the compressive strength (diametrical), flexural strength (point and three-point), tensile strength, impact strength and / or abrasion resistance.

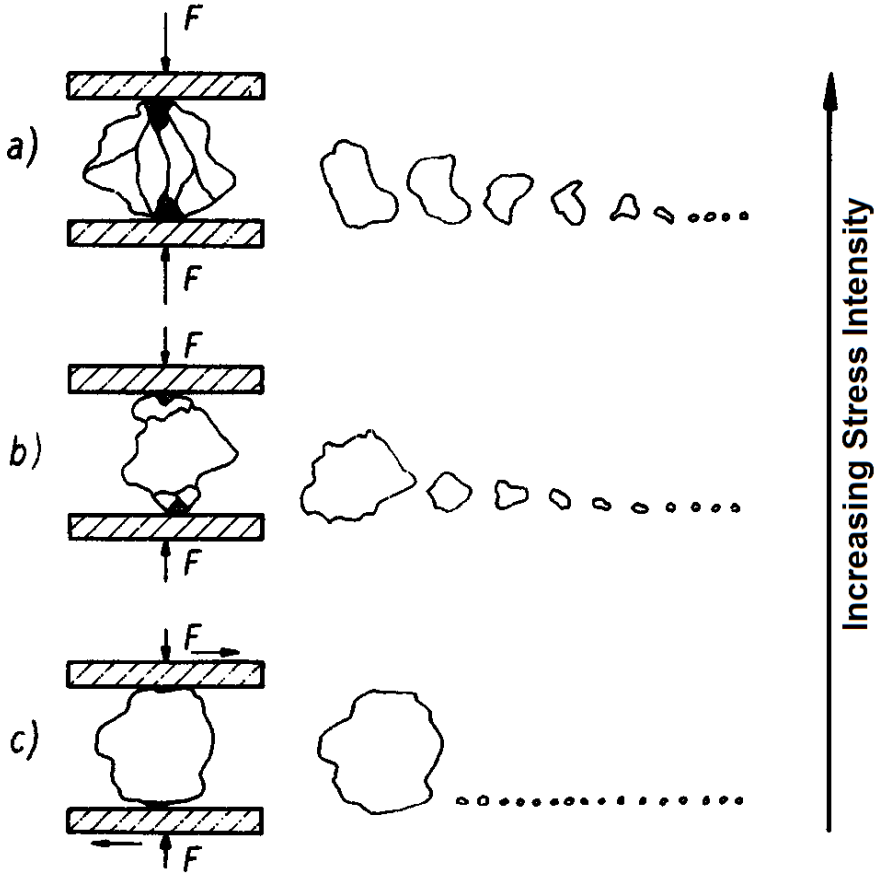


Figure 18: Influence of intensity and rate of applied stresses resulting in a) breakdown at high intensity and stress rates (shatter) b) crumble at medium intensity and speed (flakes) and c) abrasion at low intensity and stress rates (loose packed surface particles) (Schubert, 1989).

The suitability of the above mentioned test methods are dependent on the size and shape of the agglomerates. The compression strength is mainly used in most of the measurements as the tensile strength measurement is not possible for all kinds of agglomerates. The compressive strength is defined as the tensile strength perpendicular to the surface relative to the force.

Single pellets / agglomerates are subjected to fracture by applying the stresses with the help of two movable parallel plates in the **diametrical compression test method** (figure 19). This test evaluates uniaxial compression behavior of pellets. This test method is generally applied where the materials are anticipated to receive high compression forces due to live and dead loads (ex. building materials such as bricks, concrete, steel, etc.).

The test method stops / exits, when the difference in the force applied on pellets and the resistance offered by pellets exceeds 10 % especially for materials such as biomass press pellets and / or other similar deformable materials (Blumenauer, 1984).

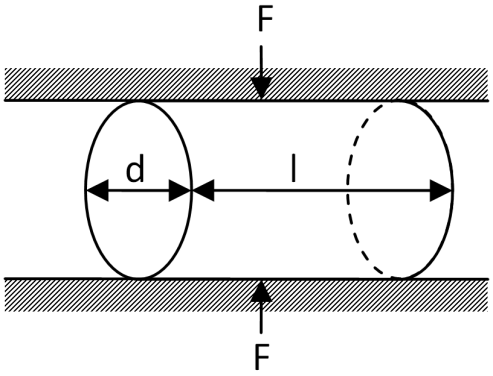


Figure 19: Schematic representation of cylindrical / diametrical compression test for agglomerates.

Point compression force is the resistance of a pellet offered towards a piercing / penetrating flattened spike. The **3-point bending force** test is the resistance of the pellet offered against fractionation through bending. The tests are carried out by applying a concentric penetrating force on the pellet either placed on a non-rollable v-shaped flat base (point) or on two edges / cantilevers supports (three-point). The test setup is shown in figure 20. It is important to ensure that the pellet is long enough to safely be located on the supports especially for the three-point tests.

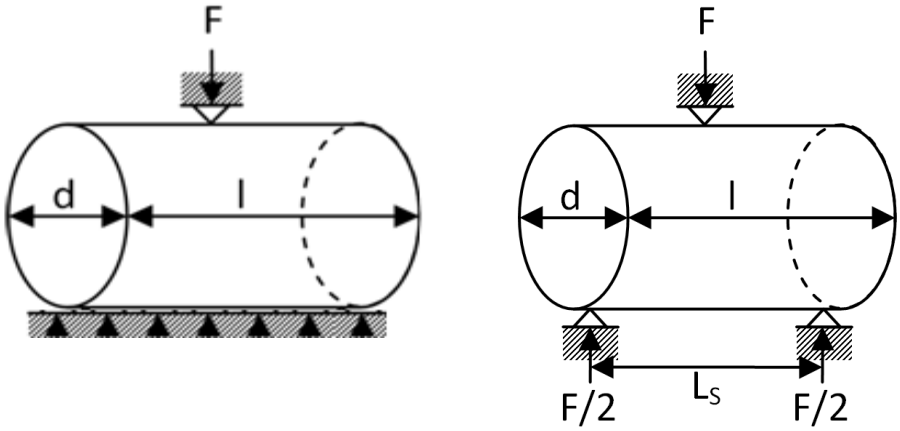


Figure 20: Schematic representation of point (left) and three-point (right) compression test for agglomerates.

The tests are run until the fracture or a predefined deflection has been measured with respect to the applied force. Stieß, (1997) states that the breaking force can be used as a representative compressive resistance force measured for similar products (biomass pellets), which have to be investigated in series.

The **impact resistance** method is used mainly for testing the toughness of metals and polymer materials. This test is also used to evaluate the quality and uniformity of different structures (Blumenauer, 1984). A sample (pellet) is fixed either on both sides or on one side (cantilevered) and is fractionated with the help of a pendulum hammer applying the force required. The pendulum hammer after release follows a circular path and releases its kinetic energy to the sample and measures the force resistance against fractionation (figure 21). The impact resistance is obtained from the difference in energy of the hammer before and after the impact with the fixed sample (pellet).

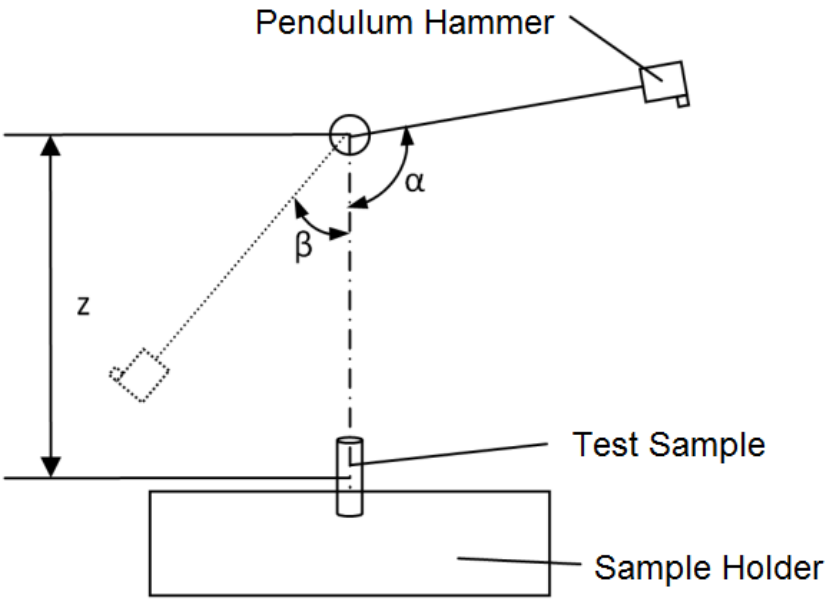


Figure 21: Schematic representation of the working principle of impact resistance test method with the help of a pendulum hammer.

The **force-displacement curves** representing different material properties are shown in figure 22. A pellet undergoes compression at stage 1 due to the increase in the force application, represented as deformation (A). Further the application of increased force results in stages 2 / 3 depending on the material behavior (elastic / plastic) starting from stage 2 on the curve. The elastic behavior is represented with deformations (B, C) observed with many tiny fissures / fractures. The plastic behavior is represented by stage 4 with deformation (D) obtained by high application of compression forces without fissures / fractures.

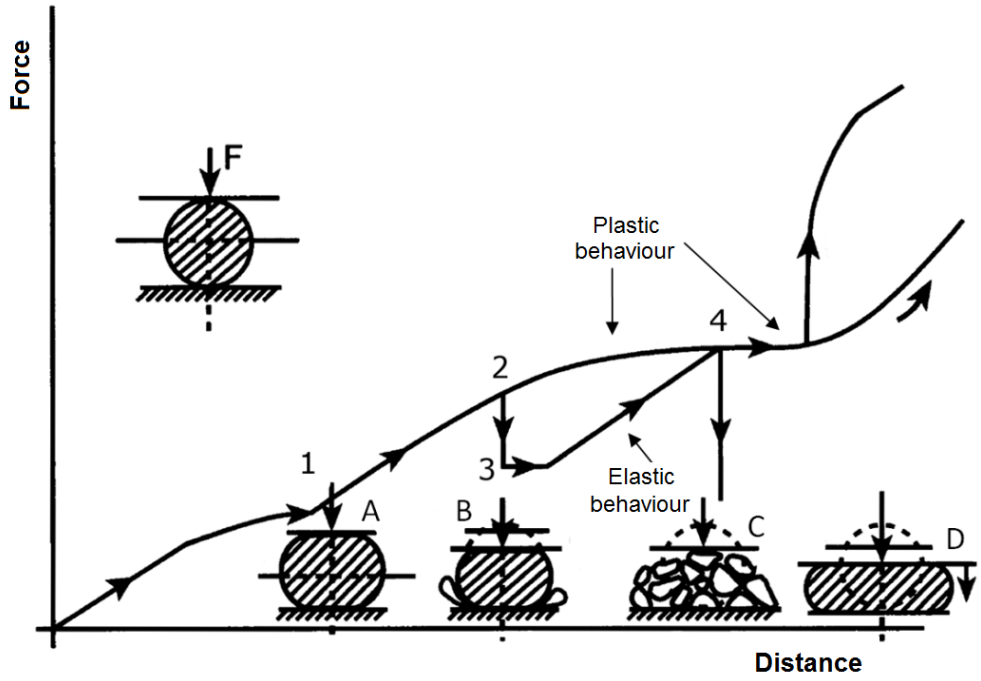


Figure 22: Force-displacement-curves with the application of compressive force in diametrical pressure test (Pietsch, 2005).

Abrasion is one of the most important parameters in the pellet production (Obernberger, 2009), which is standardized in the biomass pellet standards to be below 2.3 % and describes the cohesion / adhesion properties of highly densified particles. The abrasion test simulates the shearing and impact resistance stresses occurring in transportation, handling (feeding systems, etc.) and storage of the pellets and measures the amount of dust development. The development of dust from pellets is undesirable due to blockage of feeding systems, dust emissions, dust explosions, difficult handling for end user, loss of material, etc. (see also chapter 3).

3.0 Encapsulation

The encapsulation technology is currently applied to capture active ingredients in the pharmaceutical, food, cosmetic, colour and pigment industries. The present industries primarily utilize micro encapsulation technology for holding active ingredients and coating for macro materials for their preservation for a longer time period (www.bioencapsulation.com, last visited on 15.7.2012). Coating of macro materials is macro encapsulation. The micro and macro encapsulation processing has been carried out mainly with the help of spray nozzles either holding the materials from inside or coating the materials from outside.

Coating prevents a direct interaction of the materials with natural biological processes through which the preservation time period is extended. The current encapsulation processes are mainly based on the fabrication of hydrophobic materials coating based on their phase change characteristics. The encapsulation technology produces capsules which can be i) single or multiple, ii) porous (open) or enclosed in various sizes and shapes (spherical, cylindrical, conical, rectangular, etc.).

This thesis work intends to use the "biopolymers (renewable polymers)" as encapsulating materials, "binders" and "additives" as supporting materials in the build-up agglomeration process. Biopolymers or renewable polymers can be made from cellulose, polylactic acid (PLA), zein, poly-3-hydroxybutyrate, polyglonic acid, polyethylene, lignin, etc. and are classified under the conventions polypeptides, polynucleotides and polysaccharides.

Preferably the binders can be starch, carboxymethylcellulose (CMC), gelatin, pectin, flour, silica gel, lime, water glass, gypsum, clay, etc. and the additives are materials containing phosphorous, potassium, etc. in different concentrations. The binders are chosen such that they can bind the liquids and solids in the build-up agglomeration process. Whereas the additives are chosen to accommodate the required nutrients into the agglomerates increasing the fertilizer efficiency based on specific soil type requirements.

The **key encapsulation processes** finding their applications in the industrial practice are Particle from Gas Saturated Solutions – PGSS (Wendt et al., 2006), co-extrusion (Chemgapedia, 2012) and starch and alginate either individually or in combination (Bemiller and Whistler, 2009).

3.0.1 Particle from gas saturated solutions (PGSS) encapsulation process

The **PGSS process** (Wendt et al., 2007) permits a careful processing in an inert gas atmosphere at low temperatures, moderate pressures and is suitable for producing powders and composites of solids, very viscous melts and even liquid substances (Patent WO 95 216 88). With this technique encapsulated powders with different particle morphology and size distribution can be obtained (figure 23).

The shell material (e.g. chocolate, palm or castor fat) is melt in the vessel 1 (V_1) and the core material (e.g. liquid extracts or flavors) is filled into vessel 2 (V_2). Both the shell and core materials are heated to the designated temperatures based on their phase change characteristic and are pressurized with the help of pumps (P) into the mixing system (MS). In the mixing system (e.g. static mixer) the two substances are homogenized. CO_2 is then admixed under sufficient dissipation of energy to form micro droplets of liquid in the melted shell material. Subsequently, the micro droplets are made to expand with the help of ambient spray nozzle pressures in a spray tower (ST) forming fine droplets (Wendt et al., 2007).

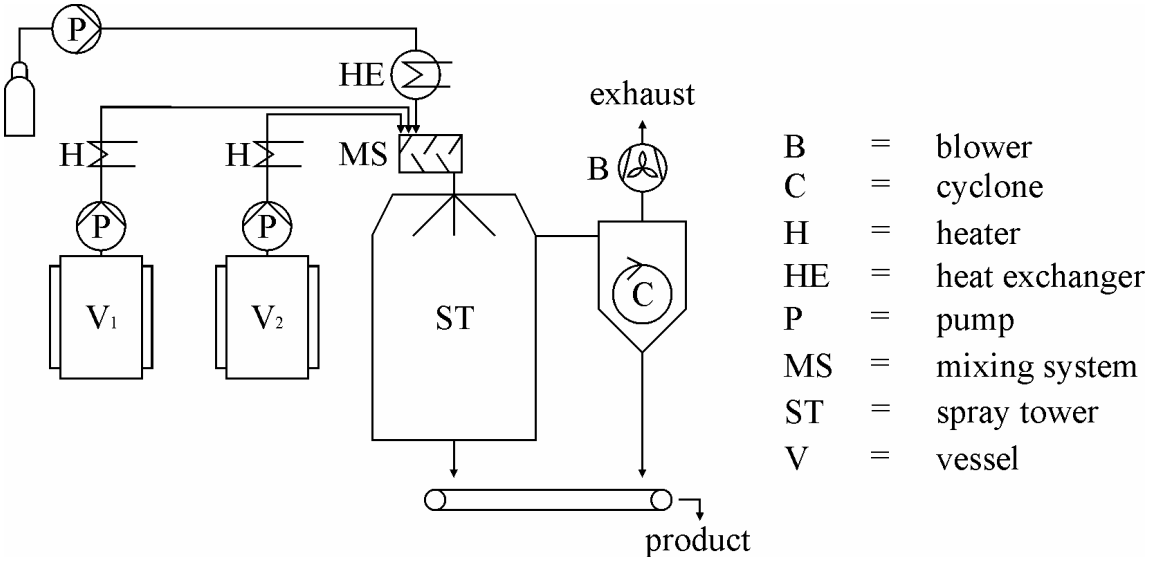


Figure 23: PGSS encapsulation process (Wendt et al., 2007).

The expanded gas increases the heat transfer from the droplets to the atmosphere very rapidly (Joule-Thomson phenomenon). This rapid heat transfer solidifies the shell material generating a powder form composite. The PGSS process uses the solidification of the continuous phase of emulsions for composite generation and produces open as well as closed composites (Wendt et al., 2007). Size and properties of the resulting capsules can be varied by varying the process parameters in dependence with the selection and properties of the materials to be utilized.

The appropriate material combinations and choice of process parameters enable the production of both open and closed composites. The application of the PGSS process has been mainly studied for solid-liquid or liquid-liquid systems with a main focus on the usage in systems of wax / polyethylene glycol, and polyester / paraffin (production of powder coatings). The injection of the material was carried out with the help of spray nozzles in a tower (Wendt et al., 2007).

The most important parameters in the PGSS process are:

- Selection and properties of materials to be utilized (core material, shell material),
- Concentration of the bound liquid,
- Structure of the mixer and the type of mixing elements,
- Selection, characteristics and quantity of the dispersion / homogenization of gas used (product gas mass flow ratio),
- Pressure and temperature before spraying and
- Temperature range in the spray tower.

3.0.2 Co-extrusion encapsulation process

The co-extrusion process (www.chemgapedia.de, last visited on 15.7.2012) is the second process for producing micro-capsules and is also based on the use of two stuff spray nozzles in a tower. This process is used especially for two immiscible components available in a liquefied state. The core material (brown colour) passes through the inner opening and the shell material (blue colour) passes through the ring-shaped gap of the nozzle (figure 24). The shell material of the capsules is conditioned (drying, cooling and chemical reactions) to improve the retention and stability.

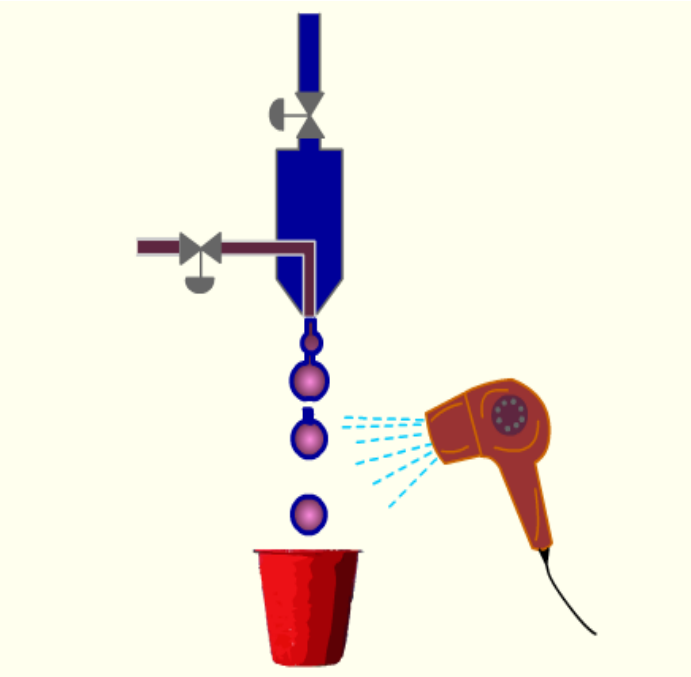


Figure 24: Micro-encapsulation in the co-extrusion process (www.chemgapedia.de, last visited on 15.7.2012).

The size and structure of the produced agglomerates / capsules depends on the properties of both the materials and process parameters. Limiting factors are mainly the process temperature (possible volatilization of easily soluble substances) and the nozzle geometry (ex. particle size in the use of suspensions). This process is applied in the production of printing inks, fragrance capsules, pharmaceutical products, cosmetic products, etc.

3.0.3 Encapsulation process with starch and alginate

The use of **starch and alginates** in combination as encapsulation materials (Bemiller and Whistler, 2009) is another possibility for the production of capsules (porous or enclosed) with the aim of integrating active substances (Whistler, 1991).

Starch consists of amylose (around 20 to 30 %) and amylopectin (approx. 70 to 80 %) together. The proportions of amylose and amylopectin vary depending on the type of starch origination (corn, cereals, tubers, etc.). Amylose is present in the form of linear helically twisted structures, whereas amylopectin is composed of highly branched structures.

The structures of starch make it possible to uptake / adsorb high water contents (swelling). The adsorption properties of starch can be improved with the help of heating (gelatinization process).

The treatment of starch with enzymes results in splitting of the structural chains and convert starch into various useful products such as glucose (G1), maltose (G2), maltotriose (G3), maltotetraose (G4), maltopentaose (G5), maltohexaose (G6), etc (figure 25). G3 and G6 are the most predominated products. G7, G8 and higher products are the hydrolyzed products with different combinations of predominated products (examples: G1+G6; G2+G5; G3+G4; G2+G6; G3+G5; G4+G4; etc.) (Bemiller and Whistler, 2009). The main enzymes involved in the breakdown of starch structural chains are amylases, isoamylases, glucanosyltransferases and transferases (Robyt, 2009).

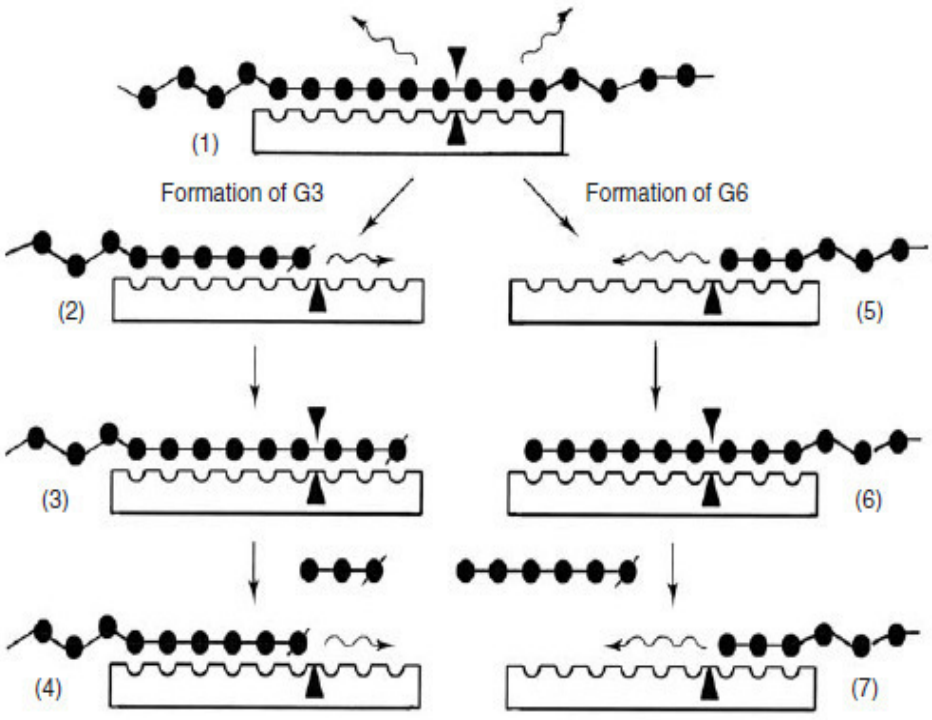


Figure 25: Hypothesis for the formation of maltotriose (G3) and maltohexaose by the dual product specificity mechanism proposed by Robyt and French, (1963).

Treatment of granular starches with the enzyme amylases (alpha-amylase or glucoamylase) below gelatinization temperature lead to the development of micro-porous granular starch matrix compositions (Whistler, 1991; Aggarwal and Dollimore, 1998; Blazek and Copeland, 2010) as shown in figure 26.

These micro-porous ring structures can store and deliver fluids to the surrounding environment in a controlled form (controlled release: open-pore system). This process mainly finds its application in the food as well as pharmaceutical industries as fluid holding medium.

Further the fluid holding capacity of the micro-porous starch granules can be enhanced with the help of surface modifying agents such as methylcellulose, polyvinyl alcohol, polyacrylamide, caboxymethylcellulose or other food grade binders / gums (Whistler, 1991). The surface treated micro-porous granules can readily absorb fatty or lipid substances including oils and creams (Whistler, 1991). This process of treating surface or starch micro-porous granules takes place for example in the production of Aqualinos (decoration spheres releasing water in controlled form) and finds its application as fluid holding medium. The retention of core materials can be increased with the help of alginate coating (Whistler, 1991; Chiu and Solarek, 2009; Bemiller and Whistler, 2009).

a) b) c)

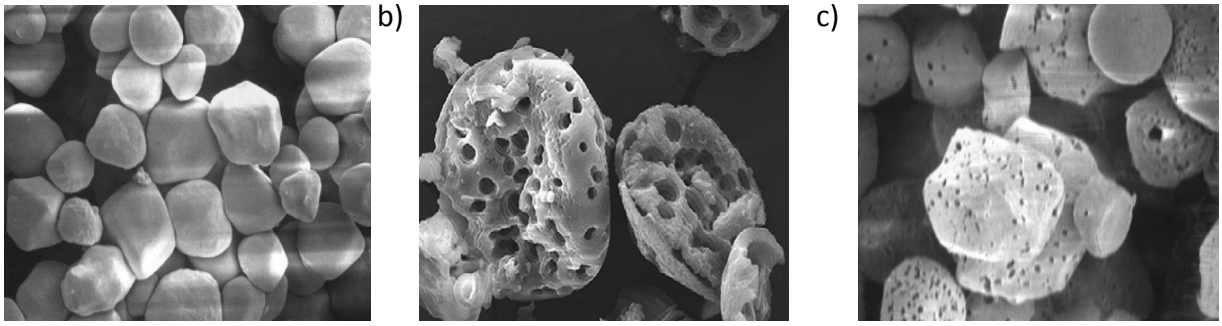


Figure 26: Microscopic observation of starch (a), and starch treated with alpha-amylase (b) (Blazek and Copeland, 2010) and glucoamylase (c) (Aggarwal and Dollimore, 1998).

Alginates (salts of alginic acid) also find its application as encapsulation material especially in the food industry (molecular cooking). Alginate is composed of a mixture of uronic, α-L-guluronic acid (Gulua) and β-D-mannuronic acid (Manua) together and are linked in varying proportions to form linear chains, which are available in the form of blocks (GG and MM blocks) (www.kimica.jp/eng-Chemical-S5htm, last visited on 10.04.2012).

The chains within the blocks are present in a structural folded form. The addition of salts (calcium or potassium chloride in aqueous solution) leads to the incorporation of salt-ions and develops into three-dimensional network structures (zigzag network structure - gelation) (Chiu and Solarek, 2009).

This process is mainly used for the encapsulation of liquid materials (medicine, food, cosmetics) and also finds application as a biopolymer (figure 27). The formed polymer layers can dissolve again under defined conditions (biodegradable).

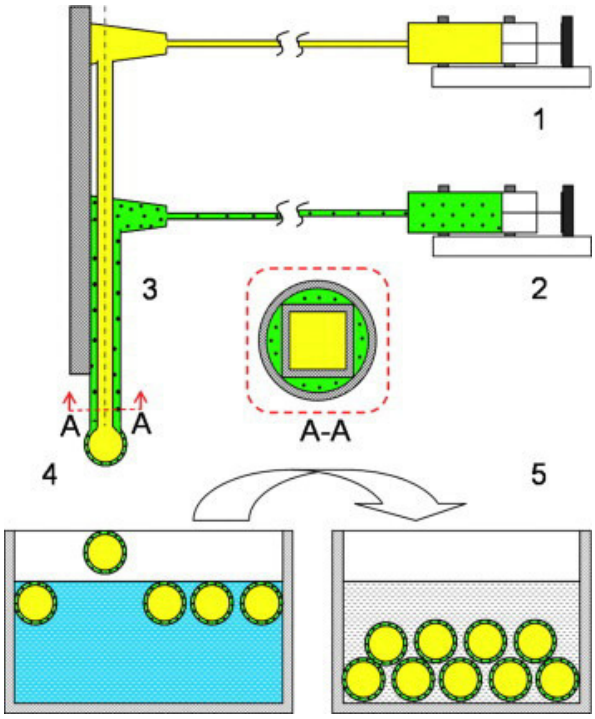


Figure 27: Schematic illustration of the process for preparation of Ca-alginate capsules with aqueous core and alginate membrane. (1) Constant flow pump for core solution; (2) constant flow pump for Na-alginate solution; (3) co-extrusion minifluidic device; (4) container of $CaCl_2$ solution; (5) container for Ca-alginate capsule storage (Wang et al., 2010).

The key **encapsulation methods (PGSS, co-extrusion, starch and alginate)** used are based on the generation of a hydrophobic shell by phase change properties of the materials (phase change material - PCM). Actual application of both the PGSS process and co-extrusion process for the encapsulation of fermentation residues is not possible / limited due to the specific requirements of i) starting liquid materials or suspensions of fine particles production, ii) operating temperatures (fermentation residues treatment below 50 °C for holding NH_4-N in the liquid phase), iii) blocking of spray nozzles due to fibrous structured fermentation residue materials.

3.0.4 Alternative encapsulation processes

Further pharmaceutical and detergent production processes also use encapsulation technology and are described briefly below. The **pharmaceutical industry** is producing capsules from years using the encapsulation technology protecting the active ingredients of drugs. The active ingredients can be dosed exactly using the encapsulation technology and are made available for the patient as prescribed. The encapsulation at the same time also reduces unpleasant taste or odor of the drugs. The pharmaceutical industry mainly uses natural macromolecular substances such as starch, gelatin and their combinations (Gstirner, 1973) making the produced capsules biodegradable.

The starch capsules in the pharmaceutical industry are produced either with single pure starch or with the mixtures of wheat starch, corn starch wheat flour, rice flour, etc. in different proportions. The capsules can be produced in different sizes and shapes with varying ingredients holding capacities. A direct filling of the starch capsules with pure hydrophilic liquid is not possible as the starch would swell and dissolve (Gstirner, 1973).

3.0.4.1 Gelatin encapsulation processes

Gelatin capsules (soft and hard gelatin capsules) in the recent decades are playing an important role in the pharmaceutical industry due to the possibility of their production in high-performance automatic machines. The soft gelatin capsules have a resilient nature, which is achieved by plasticizer such as glycerin, sorbitol or sugar solutions and are manufactured in different shapes and sizes. The capsules are preferably used as a wrapper for fatty oils, paraffin oils, essential oils, polyethylene glycols and are not suitable for hydrophilic or aqueous solutions (Gstirner, 1973).

Gelatin soft capsules are produced using SCHERER capsule machines (figure 28) producing around 100,000 capsules an hour. The two well tempered counter rotating moulds (2) are fed with soft gelatin foils (1) from both sides. Simultaneously the filling material (6) is injected with the help of a dosing feeder from top. The tempered rotating moulds in their rotation punch the gelatin foils and the capsules are manufactured. The temperature of the rotating moulds help in fusing the gelatin and by cooling the capsules regain their strength (Gstirner, 1973).

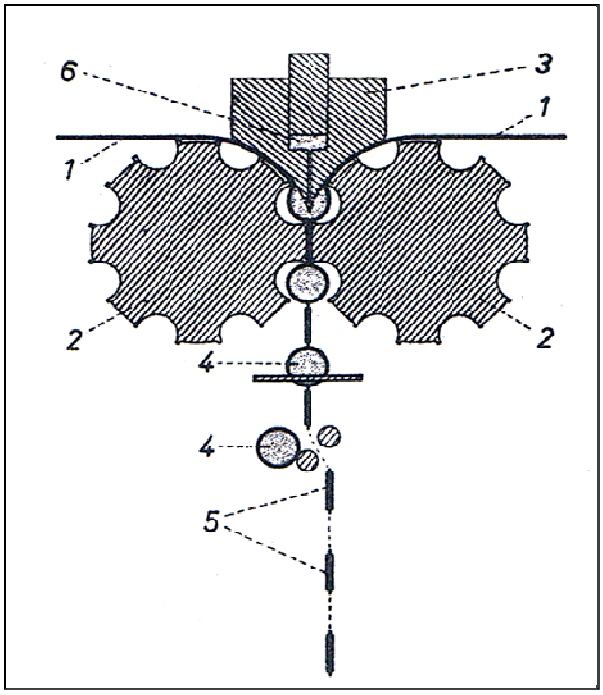


Figure 28: Working principle of SCHERER soft gelatin capsule manufacturing machine. 1) Soft gelatin tape, 2) well tempered counter rotating moulds, 3) ingredients filling wedge, 4) produced capsules, 5) gelatin tape with punched holes, 6) ingredients to be filled inside (Gstirner, 1973).

The hard gelatin capsules consist of two parts, which are bases and lids (figure 29b). These capsules are also prone to react with water and to soften themselves. The production of these capsules is carried out with the help of immersion process, where the tempered spikes are immersed into soft gelatin (figure 29a). The cooling of the immersed spikes with gelatin results into bases and lids of the capsules. The filling of the capsules can be made with the help of different filling machines (Gstirner, 1973).

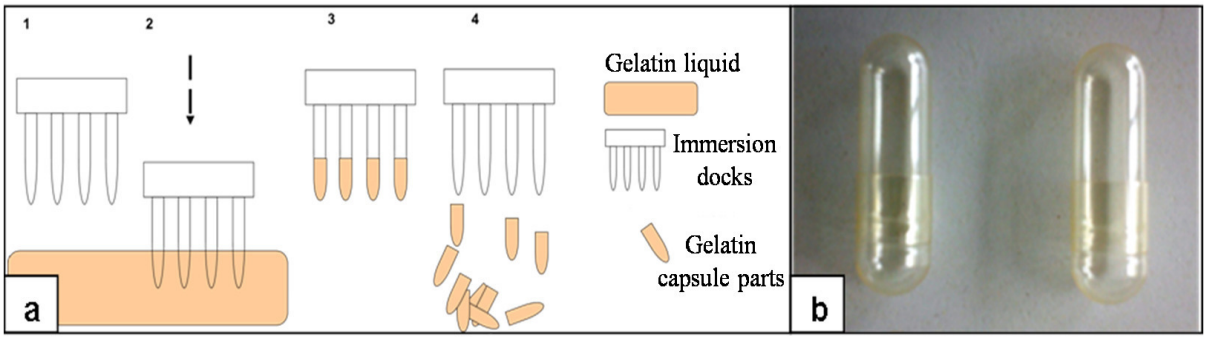


Figure 29: a) Process for production of hard gelatin capsules and b) the gelatin capsules.

3.0.4.2 Inducap® encapsulation process

The company **Inducap®** has developed a patented encapsulating method using hydraulic impulses producing spherical capsules ranging from 1 mm to 1 cm in diameters (figure 30). This method allows the production of solid macro and micro capsules of liquids or pastes. This method finds its applications in pharmaceutical as well as in biotechnological processes. In the biotechnological process it is used in immobilization of microorganisms, enzymes, yeasts and fungi (Inducap® GmbH, last visited on 15.7.2012).

This method uses two liquids, one as the core liquid (9b, 1) and the other as a wrapper liquid (9a, 3). The two liquids are stored separately in two different storage tanks (I) provided with agitators. The high-pressure pulse head (II) with the help of two alternating pulse actuators (1, 2) portions the two liquids into individual liquid volumes, which are then let to pass through an orifice / nozzle (4) with pressures developing into capsules (5). These capsules are then passed into a solidification environment (7), where they gain their strength (figure 30).

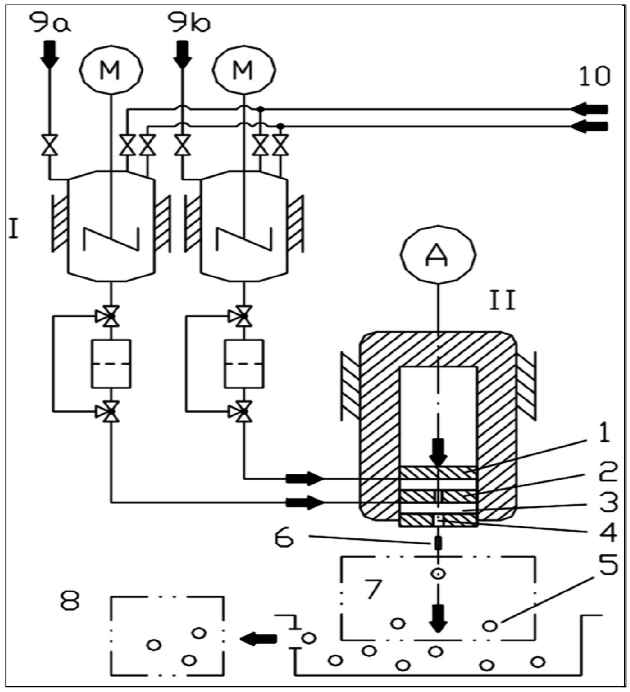


Figure 30: Schematic operation Inducap® encapsulating process (Inducap® GmbH, last visited on 15.7.2012).

Fibres can also be used as encapsulating materials for different applications, mainly applied in feed production. The Institute for Agricultural and Urban Ecology at Humboldt University in Berlin describes sugar beet pulp and fruit residues as suitable materials in the production of animal feed capsules. It is reported that sugar beet pulp and water-soluble polysaccharides of both lipophilic and hydrophilic drugs can be encapsulated at the same time.

3.0.4.3 Encapsulation with biodegradable plastics

Further **biodegradable thermoplastics** (combination of plastics and fibres) can be used as encapsulating materials. Henkel Corporation manufactures such capsules by filling in the liquid detergents (figure 31a). The shell of capsules dissolves during the washing process according to the manufacturer and is biologically safe as they are made from polylactic acids (PLA) (Henkel AG & Co. KG, last visited on 15.7.2012). The Arboform (granular form), which is mainly consisting of lignin can also be used as an encapsulating material (figure 31b) and can be brought into different shapes with the help of heat and pressure forces (Trespaphan GmbH, 2002; Gemma and Kekeis, 2005).

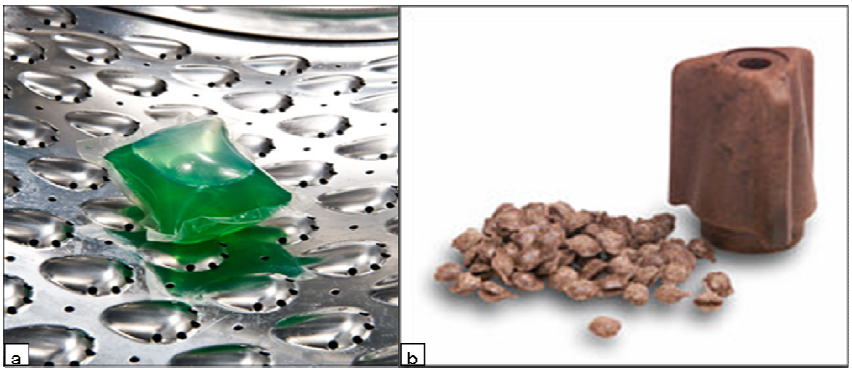


Figure 31: Biodegradable thermoplastics a) liquid-filled detergent capsules (Persil Mega-Caps, Henkel AG & Co. KG, last visited on 15.7.2012), b.) Arboform-granules (Arboform, 2012).

3.0.4.4 Coating (encapsulation) processes

Coating (immersion, thermal spraying, etc) of materials is one of the most popular encapsulating methods. Commercially available slow-release fertilizers are coated with biodegradable materials. An example is shown in the patent, entitled: "A sulfur-coated fertilizers and process for its production" (Goertz et al., 1998). This method first produces core substance granules in fluidized bed reactors at temperatures of 69 °C. Subsequently the granules are coated using pelleting discs (77 °C) into which the hot sulfur melt (152 °C) is sprayed with the help of spray nozzles. The sulfur-coated particles are then coated with biopolymers (120 °C) in the second pelleting disc.

The immersion coating process requires high adhesive material holding the core materials and offering good resistance to oils, greases, chemicals and environmental influences as well as a water repellent effect (Mammitzsch, 2009; www.wernerblank.com, last visited on 15.7.2012).

Further the patents DE 19640268 A1 (Klaus, 1998), DE 69112393 T2 (Thompson and Kelch, 1996), etc also describe the coating / encapsulation of fertilizers with latex, polyvinylchlorid (PVC), etc as "Encapsulated fertilizers with slow release".

3.0.5 Controlled release of ingredients from capsules

The **controlled release** of ingredients is directly related to the type of agglomerates (porous or enclosed, intermediate or end product) produced from the different processes (with or without dewatering, with or without grinding, with or without additives, single or multiple encapsulations, etc.) and on the biodegradability of biopolymers used. The biodegradability of the capsules in soil is ensured by the action of micro-organisms, enzymes and other bio-molecules in vivo or in vitro. The capsules enable the desired release sequence of encapsulated ingredients with respect to time (short and long-term effects) and as per requirement (fertilization effect) into the soil profile. The most important parameter for controlled release of ingredients is the permeability of the biopolymer used as encapsulating material in producing capsules. Biopolymers having water bearing characteristics release the active ingredients steadily over a long time frame.

The capsules with their above mentioned characteristics effectively increase the long time fertilization in comparison to the conventionally produced agglomerates. The controlled release characteristics of capsules also avoid / reduce the risk of water bodies and ground water contamination along with the reduction in laughing gas emissions.

3. Agricultural residues: Cereal straws (publications 1 to 3)

This chapter deals with the production of biomass pellets from stalky biomass residues such as cereal straws. The production of biomass pellets after the comminution of straw with the help of an impact mill and / or twin screw extrusion have been carried out with increasing water contents and additives with the objective of obtaining high durable straw pellets for energy applications.

3.1 Processing of cereal straws

The raw materials used in this study are straws of winter varieties of rye (*Secale cereale*) and wheat (*Triticum vulgaris*) plants. The rye and wheat were grown in the year 2005 and were harvested in the year 2006 in Goßmar, Brandenburg, Germany. The cereal straws from rye and wheat plants have been comminuted and liberated with the help of an impact mill / hammer mill as well as with a twin-screw extruder (EX) respectively.

The impact mill /hammer mill (HM) employs a high speed rotating disc to which the hammer bars are fixed (figure 32a). The hammer bars are swung outwards by centrifugal force. The material is fed into the mill through a feeder. The material is downsized by being beaten by the hammer bars in order to reduce the particle size. The material is beaten until it is small enough to fall through the sieve having an aperture size of 6 mm. The rye straw is comminuted in the industrial impact mill / hammer mill by the company Futtermittel und Dienstleistungs GmbH, Sonnewalde, Brandenburg.

The twin screw extruder (EX) works with the principle of defibration /liberation (figure 32b). Straw is fed into the twin screw extruder, where it is taken by the rotating screws. The material is brought with the rotating screws through the barrel and is compacted against a die. This helps with building up of a pressure gradient along the screws. The material gets ground in close contact between the barrel walls and the rotating screws / augers cause frictional effects and leads into shearing forces. A destruction of the material's cells occurs through the processing of moisture enriched material at high temperatures (80 °C – 130 °C) under pressure. Through high mechanical energy and high shear forces, the materials physical size (particle size) and chemical properties are changed. Through the extrusion process the straw surface gets partially destroyed which has influences on the contained lignin content and on the wax surface. The extruded material also shows a tendency to form clusters. Both rye and wheat straws are processed in the industrial twin-screw extruder by the company Lehmann Maschinenbau GmbH, Pöhl, Saxony.

a) b)

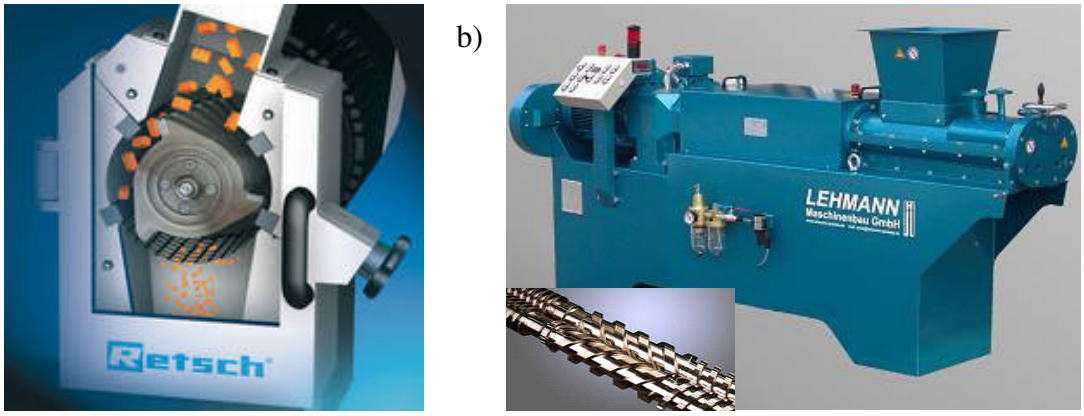


Figure 32: a) Impact mill / hammer mill (HM) and b) Twin-screw extruder (EX).

The moisture content is determined using ASAE Standard S358.2 (ASAE, 2006a), where oven drying of the samples is carried out at 105 °C for 24 h.

Particle size measurement analyses the relationship between the particle size and the amount in which the particles are abundant in the size class. The measured masses in particle size analysis are normally described as abundances r, depending on the particle number (r = 0), volume (r=3) or mass (r=3) (Stark, 2009).

The measurement results can be either displayed as fractions in quantity proportions (p_r) in the form of a histogram or as distribution sums (Q_r) in a cumulative distribution curve. A third possibility of displaying the results obtained by particle size analysis is a frequency distribution which is derived from the data of the distribution density (q_r). The method with which the particles are measured defines the abundances r. The distribution sum Q_r is defined as the partial quantities between the minimal particle size and the observed value X_i related to the total amount of the sample (Lohrengel, 2004).

$$Q_r(x_i) = \frac{\text{partial quantity} * (x_{min} \dots x_i)}{total\ amount\ (x_{min} \dots x_{max})} \quad (2)$$

The distribution density is defined as the mass percentage of the total in a defined size interval related to the interval width (Lohrengel, 2004).

$$q_r(x_i) = \frac{\text{partial quantity} * (x_{i-1} \dots x_{i+1})}{total\ amount * interval\ width} \quad (3)$$

The image analysis systems are based on particle numbers, as they work with a particle counting system, i.e. the particle distributions are given based on numerical values (Q_0 and q_0 distributions) in the image analysis systems.

The determination of particle size distribution can be carried out using different techniques (sieving, image analysis and laser diffraction). Both particle size and particle shape are important characteristics useful in analysing the quality parameters of the particles after comminution. The complete dimensions of single particles can be analyzed with the help of image analysis. The differences in particle sizes and shapes can be clearly observed after different comminution (HM and EX) processes in figure 33.

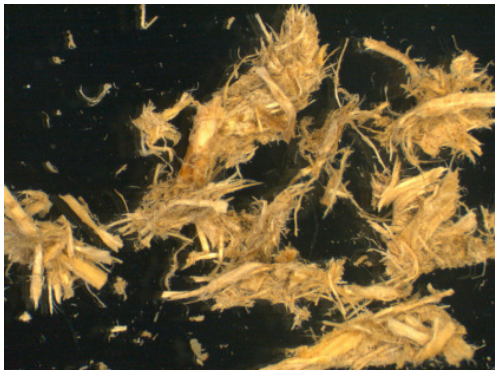
a)  b) 

Figure 33: Images of particles after different comminution /grinding processes; (a) Impact mill / Hammer mill (HM) and (b) Twin-screw extruder (EX).

To avoid the demixing and disintegration of the shredded / liberated straw, the straw material is removed from its storage barrels and laid out on a leak proof plastic sheet. The straw materials from the storage barrels are separated into four equal amounts by using a separation cross (figure 34). The two quarters of the material, located on opposite sides of the separation cross, are again separated by separation cross and this is continued till the samples are small enough to measure under image analysis system. The material is carefully separated, so that a possible loss of fine material is avoided as far as possible. The size of the separation cross decreases with the decreasing amount of material. The biggest separation cross used has a diagonal length of 100 cm, whereas the smallest separation cross used has a diagonal length of 10 cm.

Image analysis is carried out with the help of three different systems (Microscope, Fibreshape and Camsizer). Within image analysis different size characteristics (e.g. particle length, particle width) for each particle are measured.

The measurement of particle size analysis is carried out with a **Leica microscope** (figure 35a). Pictures of the static materials on the transparent bearing glass are taken in grey scale with a magnification of 6.3 %. This resolution enables to detect the smallest particle having a size of 2.7 µm. The length and width of the particles are computed by the longest and shortest Ferret diameter of the particles. Detection of the particles is carried out manually for the exact measurement of particles. Detection is the process of distinguishing between wanted and unwanted regions in a field or between image details and the background based on the grey level of each pixel.

Figure 34: Sample preparation for particle size analysis using a separation cross.

Static image analysis is carried out with the help of **Fibreshape** from Innovative Sintering Technologies (figure 35c) using a flatbed film scanner at a resolution of 1200 dpi. These settings enable to detect the particles having a size equal to or bigger than 21 µm.

Dynamic image analysis is carried out with the help of **Camsizer** from Retsch Technologies (figure 35b). The Camsizer is an optoelectronic device for the measurement of particle size distribution of dispersed materials. The elements that are used for the particle analysis within the Camsizer system are the extended light source and two CCD (charged coupled device) cameras with objectives for taking pictures of the shadows of free falling particles (Retsch Technology, 1999). The Camsizer can detect particles having sizes in between 19.7 µm and 30 mm.

The assessment of particle size distribution is carried out with three representative samples for each variant with each of the image analysis systems. Each sample on average has a minimum of 3,000 particles for Microscope, 30,000 particles for Camsizer and 16,000 particles for Fibreshape respectively.

Respective straw pellets are produced after the determination of particle size distribution analysis from different comminution processes. Pellets in this work are first prepared directly from the comminuted straws and secondly with the admixture of additives (biogenous and fossil) to the comminuted straw. The mixtures are mixed together with the help of an Eirich-intensive mixer to obtain a uniform mixture (see chapter 5).

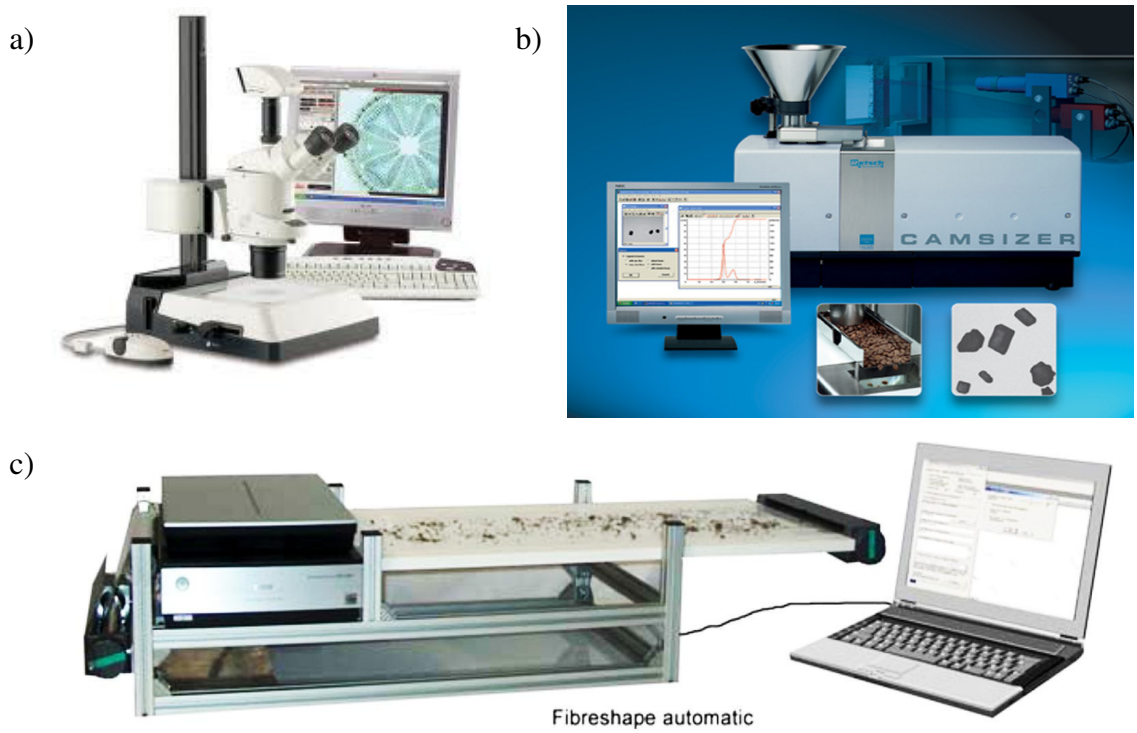


Figure 35: Leica microscope (a), Camsizer from Retsch Technologies (b) and Fibreshape from IST AG (c).

The biogenous and fossil additives are chosen in such a way that these additives have a higher heating value compared to the rye and wheat straws improving the heating value of the pellet blends. Paraffin (48 MJ kg^{-1}) and palmitin (38.83 MJ kg^{-1}) are added as biogenous additives, whereas anthracite coal (27.89 MJ kg^{-1}) and lignite (21 MJ kg^{-1}) coal are added as fossil additives. The blend mixtures are only prepared with rye straw based on the anticipated heating values (18 MJ kg^{-1} and 18.5 MJ kg^{-1}) and are given in table 6.

In order to achieve the optimized pellets, the raw materials wheat straw, rye straw and their blends are prepared with increasing water contents starting from 14 wt. % (table 7). This is carried out by first measuring the water content of the raw materials / the mixture blends, and thereafter additional water is supplied in the mixing process. The water is supplied as a binding agent in the pelletisation of the raw materials. The moisture content greater than 14 wt. % is used based upon the literature review as this moisture level would produce high density and better quality pellets from various straws (Kaliyan and Morey, 2006; Mani et al., 2006; Obernberger and Thek, 2004; Shaw and Tabil, 2007).

Table 6: Blend mixture ratios of straws with biogenous and fossil fuel additives calculated based on the anticipated heating value between 18 MJ kg^{-1} and 18.5 MJ kg^{-1}.

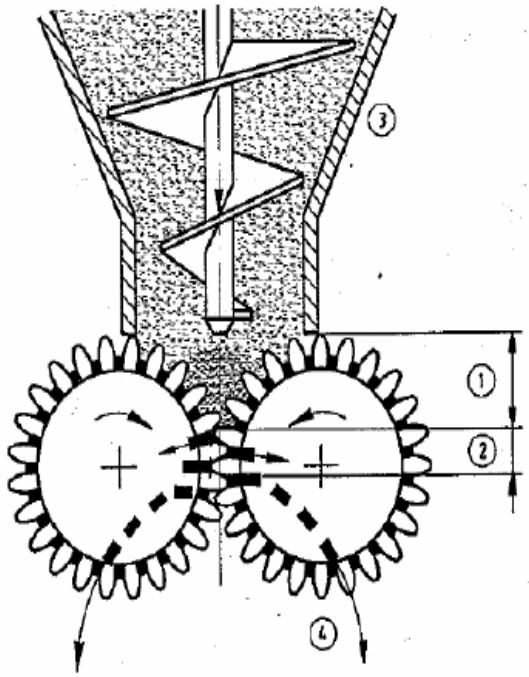
Raw materials	Heating values	Mixture ratio (%)		Heating value of mixture
	(MJ kg^{-1})	Straw	Additive	(MJ kg^{-1})
Rye straw	17.2	100	--	17.2
Wheat straw	17.4	100	--	17.4
Paraffin	45.0	95.32	4.68	18.5
Palmitin	38.83	93.99	6.01	18.5
Anthracite coal	27.89	87.84	12.16	18.5
Lignite coal	21.00	65.79	34.21	18.5
Lignite coal	21.00	79	21.00	18.0

The water content is varied in percentage to develop the optimal mixture to achieve lower abrasion and higher strength of pellets. The water content of the straw measured is in between 6.5 and 8.7 wt. % after the respective comminution processes. The additional water ranging from 5.3 to 7.5 wt. % is supplied in to the mixing apparatus for obtaining a total water content of 14 wt. %, and is respectively investigated for the remaining water contents. The blend mixtures with varying water contents are prepared by supplying the additional water required for individual mixtures after measuring the water content of the mixtures respectively.

Table 7: Pelletisation of cereal straws and their blends with respect to the increasing water contents starting from 14 wt. %.

Raw material (wt. %)	Symbol	Water content (wt. %)						
		14	15	16	17	18	19	20
Rye straw (100 %)	RS	X	X	X	X	X	X	X
Wheat straw (100 %)	WS	X	X	X	X	X	X	X
Straw (95.32 %) + Paraffin (4.68 %)	P1	X	X	X	X	X	X	X
Straw (93.99 %) + Palmitin (6.01 %)	P2	--	X	X	X	X	X	X
Straw (87.84 %) + Anthracite (12.16 %)	AC	--	--	X	X	X	X	X
Straw (65.79 %) + Lignite (34.21 %)	LC1	--	--	X	X	X	X	X
Straw (79 %) + Lignite (21 %)	LC2	--	--	X	X	X	X	X

Pelletisation is carried out with the help of a laboratory compactor (Hosokowa Bepex, Type L200 / 50G + K). The working principle of the compactor is similar to that of a hollow roller press. The material is auger fed towards the working area of the roller moulds, where it is pressed and the materials passes through the mould openings (figure 36). Densification of the raw materials /raw material blends takes place in the moulds. The mould openings are 25 mm long and have a diameter of 8 mm. The temperature measured during the pelletisation process is between 80 °C and 100 °C.



1. Densification zone
2. Pressure zone
3. Auger feeding
4. Pellets

Figure 36: Hosokowa Bepex laboratory compactor (Type L200 / 50G + K) with the working principle.

The rye straw, wheat straw and their blended pellets are stored for 14 days at a temperature of 20 °C such that the water content of the pellets stabilizes. Abrasion tests and strength tests are carried out after the stabilization of the water content in the pellets.

Pellet density is measured as the ratio of mass of pellets in a predefined volume to the volume. The higher the pellet density, the higher is the energy density and the lower are the transport and storage costs. The pellet density is determined using a cylindrical vessel having a measuring volume of 56.15 l (D*H: 38*49.5 cm^2) as per the standard ASAE S269.4.

The abrasion of pellets is one of the most important parameters in the pellet production. Abrasion is an essential criterion to be considered by the end user as a lower abrasion value produces less particulate emissions, has lower transportation losses and prevents bridging (formation of clusters of irregular size and shape) of particles during storage (Obernberger and Thek, 2002). A high amount of fines in the pellets can cause failures in the feeding system.

Abrasion has been measured using two different tumbling devices as per the standards ASAE S 269.4 (Pfost pellet tester: quadratic crate) and SS 187120 (octagonal crate). The ASAE S 269.4 is a tumbling device made of a rectangular container with inner dimensions of L*B*D: 30*30*12 cm^3 (figure 37a). The tumbling effect is enforced with a 23 cm long baffle placed diagonally having an extension of 5 cm into the crate. The container / crate is rotated perpendicular to the sides of the container. The durability tester as per SS 187120 (figure 37b) is a tumbling device having octagonal shape (L*D: 18*12 cm^2) without any baffle. The durability tester is then modified with one baffle (figure 37c) and then with two baffles (figure 37d) meeting in the centre and being perpendicular to each other. The baffles are having a length of 23 cm and a projection of 5 cm into the crate. The baffles in both the tumbling devices create a fractionation effect in the pellets.

The durability tests with both tumbling devices are carried out with varying rotation times (5, 10 and 20 min) and with varying mass of pellets (100, 150, 250, 500 and 1000 g). The tumbling devices are made to rotate at a speed of 50 rpm for the specified time with a specified mass of pellets. The samples are then sieved with a sieve having an aperture of 6.3 mm (0.8 * pellet diameter) as suggested by Thomas and Van der Poel, (1996). The difference in the weights of the pellets before and after the abrasion test results in the abrasion value.

The strength indicates the quality of pellets. The quality of pellets is noticeable by an exceptionally smooth pellet surface without any fissures. Moreover stronger pellets develop less particulate matter during handling. The strength tests (diametrical pressure test, point pressure test and three-point bending test) are carried out with the help of a ZWICK-ROELL (type: ZMART.PRO) material testing (tensile and compressive strengths) machine (figure 37e). These pressure tests are selected and imposed as such pressures occur during handling, transportation and storage of the pellets.

Pressure tests are carried out via different strength parameters (diametrical, point, 3-point, impact). The pressure testing methods are explained in chapter 2. The strength of the pellet is measured as the pressure strength which the pellet can withstand without breaking.

Impact resistance of the pellets is measured using dynamic pressure tests (type: Ceast Resil 5.5). The impact resistance is measured by the difference in kinetic energy of the falling pendulum hammer caused by the resistivity of pellets against the impact. The impact resistance gives the energy required in the destruction / fractionation of pellets (see also chapter 2).

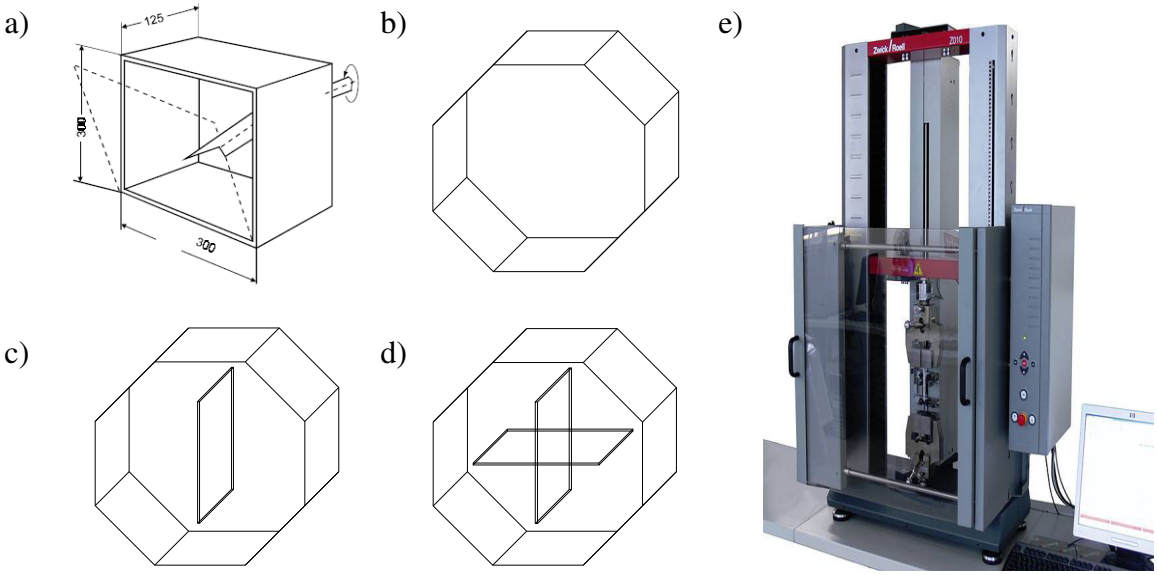


Figure 37: Different abrasion (tumbling devices as per ASAE S 269.4 (a) and SS 187120 (b)) and strength testing machine (e) (from Zwick-Roell type: ZMART.PRO). Further the modification of SS 187120 with one (c) and two baffles (d).

The strength tests three-point bending pressures and impact resistance require the pellets to have a certain length. The length of the pellets as per the pellet standards is specified to be five times the diameter. The pellets prepared have 8 mm diameter and 40 to 50 mm length. These size properties are sufficient enough for carrying out the strength tests. The strength of the pellet (F) is dependent on the surface tension of the binding liquid (γ) and the radius (r) of the neighbouring particles (equation 4).

$$F = \Delta p = 2 * (\gamma/r) \quad (4)$$

3.2 Results and discussions based on the processing of cereal straws

The water content of the rye and wheat straw are in between 6.5 and 8.7 wt. % after the comminution processes. The pellets are prepared with increasing water contents starting from 14 wt. %. The water content of the straw pellets and their blends measured after stabilization (14 days at 20 °C) is in between 8.3 and 10 wt. %. The water content in the pellets after stabilization is below the value mentioned under the standards for wood pellets. The 10 wt. % water content improves the durability of the pellets (Kaliyan and Morey, 2009; Nielsen et al., 2010). The water content has an influence on the net calorific value, combustion efficiency and the temperature of combustion (Obernberger and Thek, 2002; Nussbaumer and Kaltschmitt, 2001).

Higher water content reduces the durability and energy efficiency of the produced pellets. The optimum water content for pellets should be less than 10 wt. % as specified in standards (DIN 51 731, DINplus, ÖNORM M 7135). Kaliyan and Morey, (2006b); Mani et al., (2006a); Obernberger and Thek, (2004); Shaw and Tabil, (2007) state that the 10 wt. % moisture content of pellets would result in longer storage and high combustion efficiencies, through which a high energy efficiency can be achieved.

Water as a binding agent distributes itself around the particles without damaging the already existing bonds. This distribution of water helps in bringing the neighbouring unbound particles together due to the formation of liquid bridges at the contact points. The elevated temperatures in the pelletisation / densification processes cause redistribution of the water via evaporation and condensation leading towards an increased mobility of water. The mobility of water in the pelletisation processes shrinks the moisture bridges and thus helps in increasing the strength and stability of the pellets.

The particle size analysis (Q0: length and width) after the comminution process are depicted in figure 38. The distribution curves start from 30 µm as the lowest resolution value of the three image analysis systems is 21 µm. An identical particle size distribution is observed from the two different comminution processes (impact mill and twin-screw extruder) for the rye and wheat straws. The results show differences in the length and width distributions of the particles measured with different image analysis systems.

Particle size and shape distribution influences the bonding characteristics and help in continuous processing of the materials (straws) without blocking the moulds / dies. The pellets produced after the straw comminuted with twin-screw extruder results in high durable pellets due to higher binding characteristics.

Particle size distribution also affects the combustion process. Small particles and fines have higher burning rates and ignition front speeds (Ryu et al., 2006). Larger particles are thermally thick having slow devolatilization rate and more distributed heat transfer to the nearby particles. Ryu et al., (2006) states that with the increase in particle sizes (from 5 mm to 35 mm) there is a decrease in burning rate and also a decrease in heat influx from larger particles to the smaller particles and fines.

The Q0 results (figure 38) show that 60 % to 80 % of the particles can be classified into smaller particles and fines (< 600 µm), indicating that the burning rate and the heat influx would be optimal in the combustion process.

Fines are rich in lignin content originating from the middle lamella of fibres and act as a natural binder. This binding of lignin increases the stability and strength of the pellets. 20 % to 40 % of the particles are classified as fibrous particles (> 600 µm), which intertwine with each other during pelletisation and act as an additional binding feature (Gilbert et al., 2009). The distribution of fines and fibres should be in good proportion in order to achieve optimal bonding, as this relationship improves the pellet quality such as density, stability and strength characteristics.

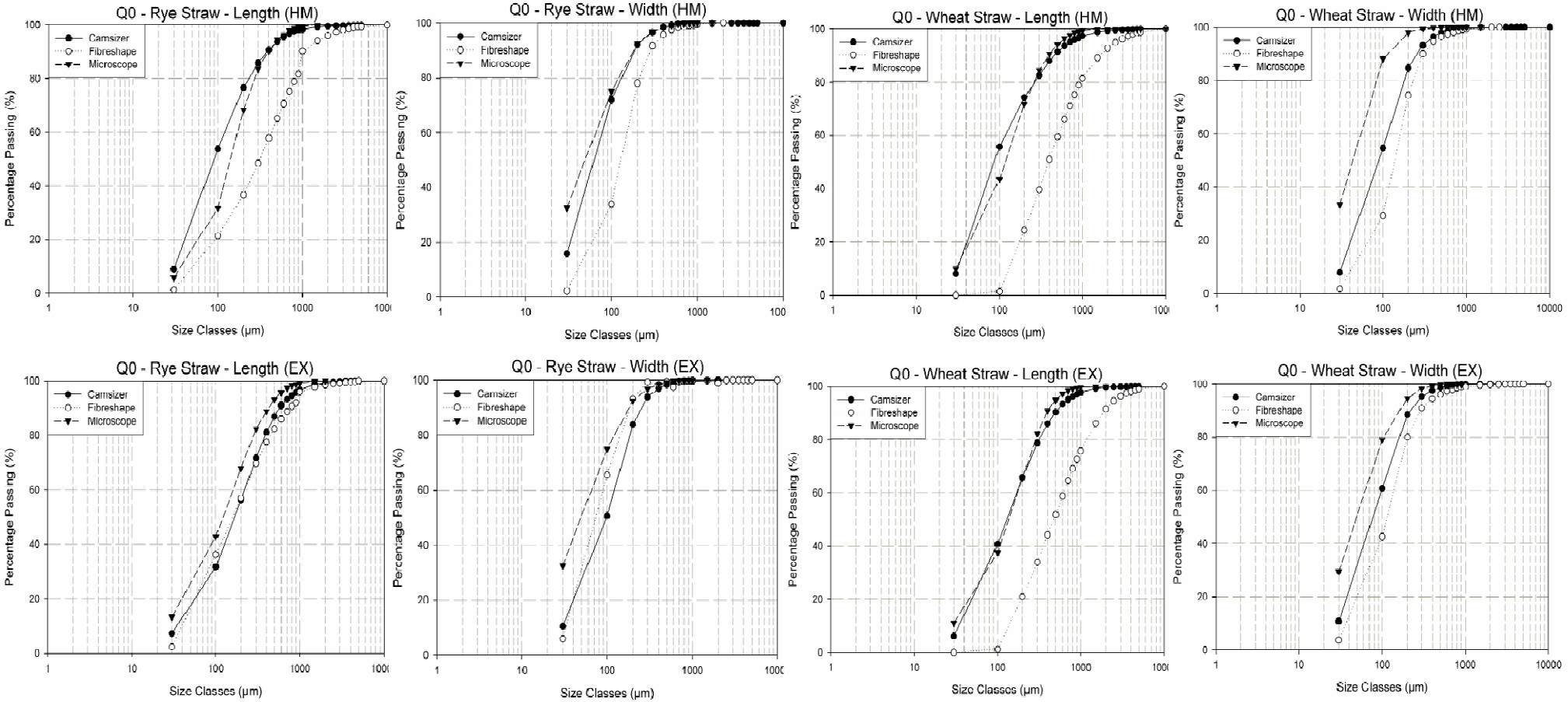


Figure 38: Particle size analysis (Q0) of the rye and wheat straw after two different comminution processes (HM and EX) analyzed with three different image analyses systems.

Further particle size analysis is also carried out for the biogenous and fossil additives as well as for the thereof produced blend mixtures enhancing the pellet properties (figure 39). The particle size analyses of the additives and their blend mixtures are compared with the particle size of rye straw comminuted with an impact mill / hammer mill. The fines in the lignite and anthracite dust are ranging in between 40 % and 60 %. The particle size distribution of the mixtures LC1, LC2 and AC are similar to that of the straw particle distribution without additives and show a ratio of 20 % fines and 80 % fibres.

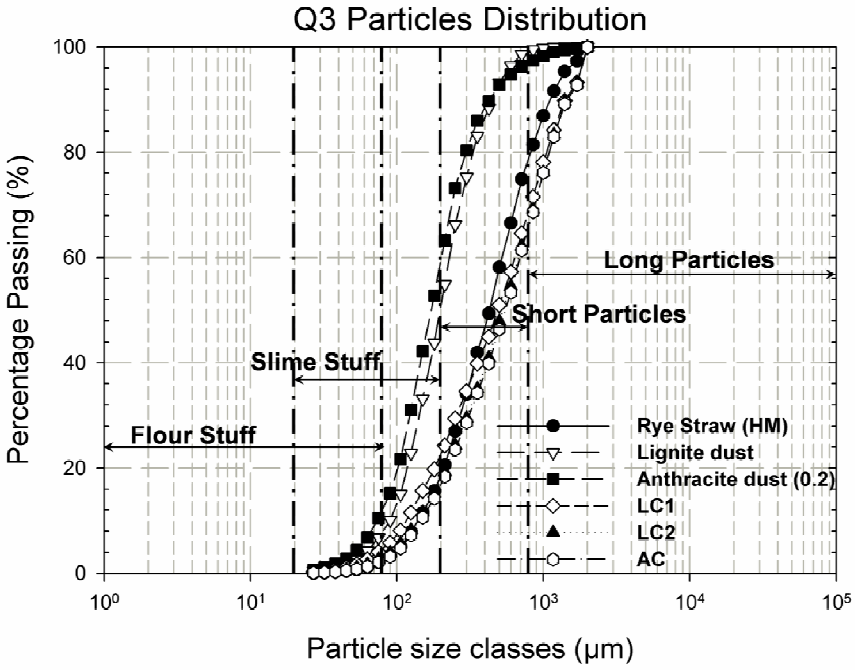


Figure 39: Particle size distribution of the rye straw, additives and the rye straw – additive mixtures.

The important fuel property which changes with the pelletisation is the bulk density of the raw materials (Ryu et al., 2006; Gilbert et al., 2009). The straws generally have very low bulk density values usually ranging in between 40 and 150 kg m^{-3} including baled density (Kaliyan and Morey, 2009). The measured bulk density of the straw pellets is 545 kg m^{-3}, whereas the blended straw pellets on average are ranging in between 572 and 667 kg m^{-3} (figure 40). The increase in bulk density significantly reduces the costs for storage, transportation, handling, feeding of the biomass and also increases the energy density.

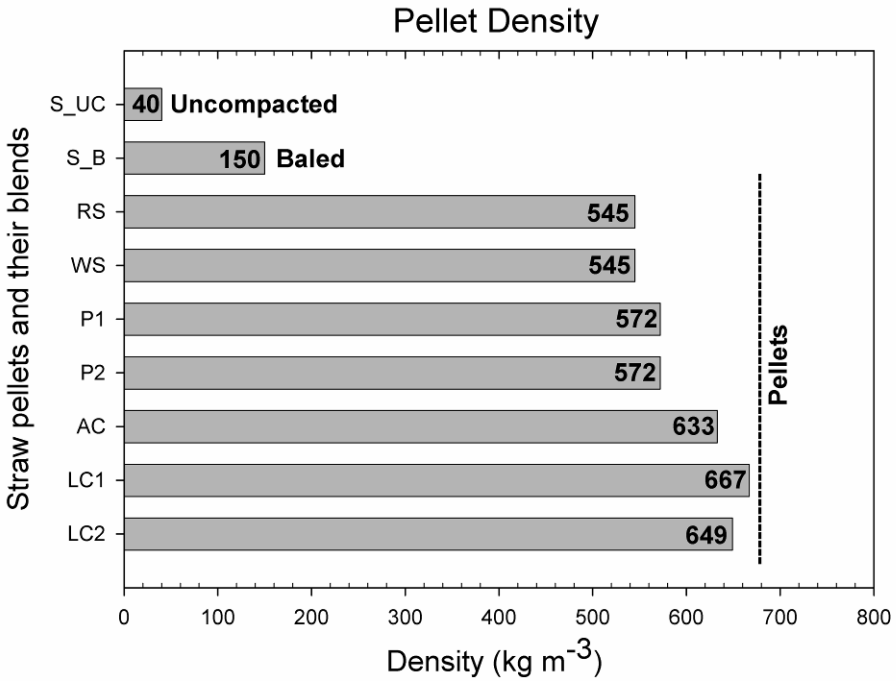


Figure 40: The density of straw pellets and their blend pellets measured after stabilization of water content as per standard ASAE S 269.4.

The usage of cereal straws and their blends as a source of energy is dependent on its characteristics. The chemical characteristics of cereal straws (RS and WS), additives (biogenous and fossil) and their blends are given in table 8. The carbon (C), hydrogen (H) and nitrogen (N) values in the cereal straws comply with the natural ranges of the raw materials (Obernberger and Thek, 2002). The optimal value of N should be less than 0.3 % as per standards DIN 51731, Ö NORM 7135, EN 14961. However the values of N in the rye straw analysed are above 0.3 %. The values of N in the straw pellets and blend pellets analyzed are in between 0.3 and 1.5 % compared to that of the wood pellets with 0.1 % (Schaffenberger and Stastny, 2008). The standards Agro+ and Agro specify that the N values can range up to 1.5 % and 2.0 % respectively. The N values of the produced pellets ranging in between 0.3 % and 1.5 % suit as per the standard Agro+ to be used as a fuel.

C, H and oxygen (O) are the main components of the biomass fuels; C and H are oxidized during combustion by exothermic reactions and therefore influence the calorific value of the fuel. The organic O provides a part of the O for the combustion process. Additional O must be supplied by air injection in the furnace (Obernberger and Thek, 2009).

As per the standard DIN 51731, the values of chlorine (Cl) and sulphur (S) should be less than 0.03 % and 0.08 % respectively. The values of Cl and S obtained in the straws and their blends are above the values specified in the wood pellet standards, but are below the specified values in the agricultural residue (Agro+ and Agro) pellet standards (≤ 0.2 %). The concentrations of Cl and S should be limited as they have negative influences on the combustion processes. High amount of S and Cl can cause problems in emissions (SOx), depositions and corrosion (HCl) of the furnace.

The heating value of the rye and wheat straw can be calculated based on the chemical composition of the raw materials using equation 5 (Kaltschmitt et al., 2009). The water free (wf) heating values are calculated for the cereal (17.2 and 17.4 MJ kg^{-1}) straws, biogenous (45 and 38.83 MJ kg^{-1}) and fossil (27.89 and 21 MJ kg^{-1}) additives using the equation 5 (Kaltschmidt et al., 2009).

$$H_{u(wf)} = 34.8*C + 93.9*H + 10.5*S + 6.3*N - 10.8*O \quad (5)$$

Table 8: Chemical characteristics of the straws, additives and their blend mixtures calculated based on the mixture ratios.

Raw material	Heating value (MJ/kg)	Volume % of dry mass					
		C	H	O	N	S	Cl
Rye straw	17.4	46.6	6.0	42.1	0.55	0.085	0.19
Wheat straw	17.2	45.6	5.8	42.4	0.48	0.082	0.19
Paraffin	45.0	19.4	40.8	--	--	--	--
Palmitin	38.83	18.5	35.0	4.4	--	--	--
Anthacite	27.89	72.5	5.6	11.1	1.3	0.94	0.1
Lignite	21.0	65.9	4.9	23.0	0.7	0.39	0.1
P1	18.5	45.6	8.3	39.5	0.42	0.1	0.1
P2	18.5	45.2	8.4	39.2	0.41	0.09	0.1
AC	18.5	50.01	6.6	37.7	0.54	0.2	0.11
LC1	18.5	49.6	5.6	39.8	0.55	0.15	0.1
LC2	18.0	48.9	5.3	37.5	0.49	0.16	0.11

Another characterization of cereal straws is the definition of the ligno-cellulosic composition. Lignin plays an important physiological role in plants as it works as an adhesive between fibres. In biomass pellets, lignin acts as a binding agent (Oliviera et al., 2009; Gilbert et al., 2009). The lignin polymer gives firmness to the pellets, through which the durability characteristics of the pellets can be improved (Obernberger and Thek, 2009). Chen et al., (2007) states that agricultural straws contain about 10 to 27 % of lignin. The lignin content in the rye and wheat straw are 26 % and 27 % of the dry matter.

Obernberger and Thek, (2009) state that the lignin polymer softens at a temperature of 190 °C. The softening temperature of lignin reduces with increasing water content in the biomass. The water content of straw measured is in between 6.5 and 10 wt. %. With 10 wt. % water content, the softening temperature of lignin reduces to 130 °C. The pellets are prepared with water as a binding material starting with 14 wt. % water content, indicating the lignin softening temperature to be in between 80 °C and 100 °C (Gilbert et al., 2009; Obernberger and Thek, 2009). The temperature of the rotating moulds of the compactor measured is in between 85 °C and 100 °C, indicating that the lignin is softened and helped in the firmness of the pellets after conditioning.

Gilbert et al., (2009) observes that the firmness and bulk density of the pellets increases with increasing temperatures from 60 °C to 100 °C and noticed a decrease in firmness and bulk density with further increase in temperatures from 100 °C to 130 °C. The moisture in the pellets evaporates completely when the pellets are prepared above 100 °C and affects the quality of the pellets negatively. The complete evaporation results in harder and brittle pellets, which easily deform and have low strength. Special care is taken so that the temperature of the rotating moulds does not reach a value higher than 100 °C, with which it is assured that the pellets are prepared under the optimum conditions.

The pellets are prepared with increasing water contents starting from 14 wt. %. The pellets are then tested for abrasion and the optimal water content is determined with respect to the minimum abrasion values achieved. The abrasion (mechanical strength) of pellets is one of the most important parameters in the pellet production. Abrasion is the percentage of fines returning from the pellets after being subjected to mechanical or pneumatic agitation. Abrasion is an essential criterion to be considered by the end user as lower abrasion value produces less particulate emissions, has lower transportation losses and prevents bridging (clusters of irregular size and shape) of particles during storage (Obernberger and Thek, 2002). A high amount of fines in the pellets can cause failures in the feeding system.

The minimum abrasion values of rye and wheat straw pellets with the quadratic crate (ASAE S269.4) are obtained at 17 wt. % and 18 wt. % water content in the mixture (figure 41a). This 17 wt. % water content is considered to be the optimum water content and 16 wt. % is chosen as the starting water content in preparing the cereal straw blend pellets. Low abrasion values are recorded for the straw pellets and their blends measured with the octagonal tumbling crate as per standard SS 187120 (figure 41b).

An increasing abrasion is observed with increasing baffles in the standard SS 187120 octagonal crate (figure 41c and figure 41d). Figure 41e shows the pellets before abrasion with glassy surface structure, where as figure 41f shows the pellets after abrasion. The size of the pellets is reduced after abrasion, which can be due to the fractionation of pellets with the baffle. Further the pellets after abrasion also display a rough surface, which can be due to the rotational frictional forces acting on the pellets from the tumbling crate walls.

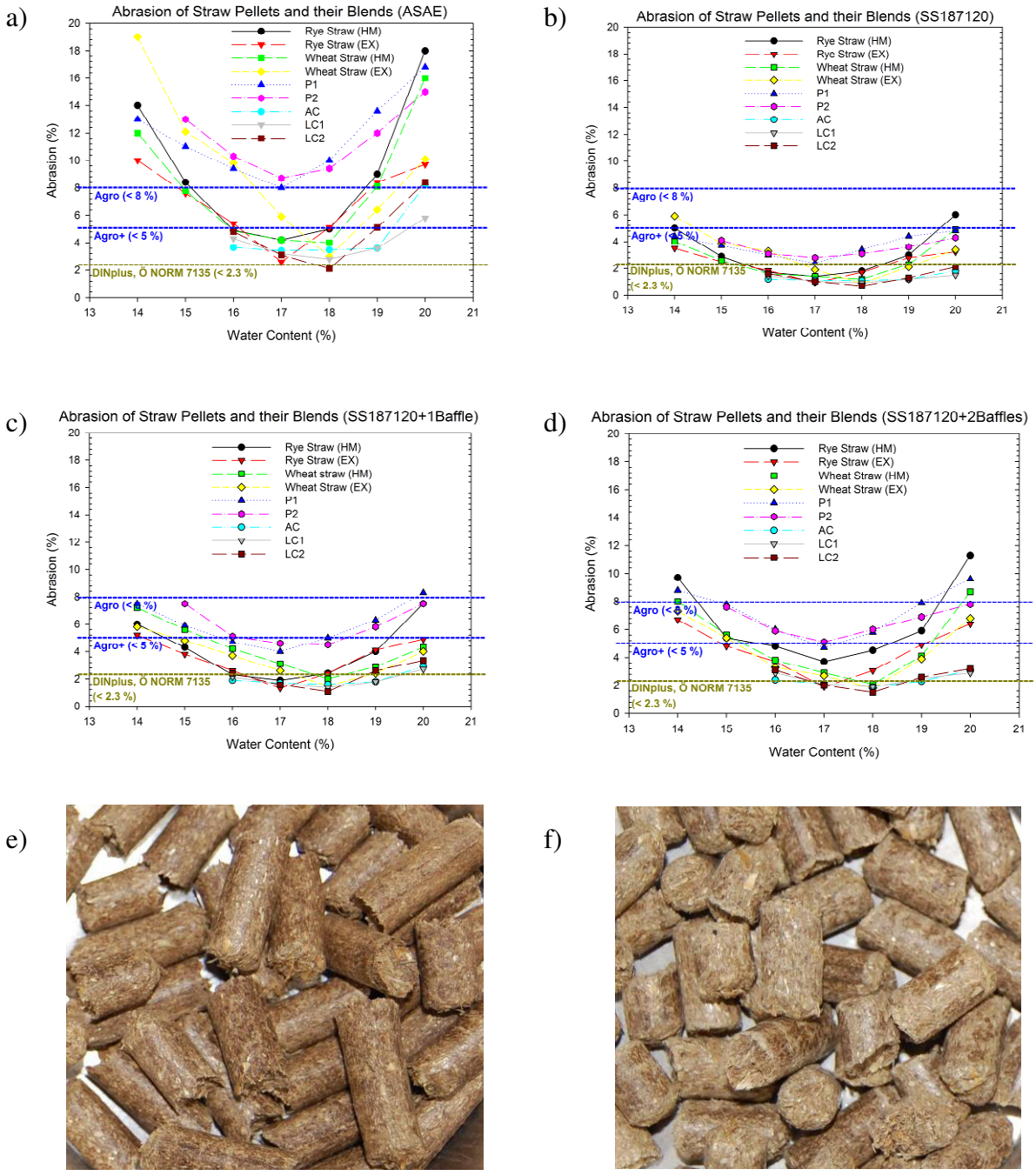


Figure 41. Abrasion of the cereal straw pellets and their blends prepared with increasing water contents after two different comminution processes as per the standards ASAE S269.4 (a) and SS 187120 with (c and d) and without (b) modifications. Pellets after stabilization (e) and after the abrasion test (f).

Further the effect of time on the abrasion of pellets is noted with varying rotation times (5 min, 10 min and 20 min) of both the tumbling devices. 10 min is given as the standard time as per the specified pellet standards. The results show increasing abrasion values with respect to the increasing rotation times in the tumbling devices (figure 42). The higher (20 min) tumbling time is chosen as pellets in their different handling processes undergo stresses for longer than 10 min. The lower tumbling time is chosen to check the effect of short handling stresses when the pellets are handled for short times.

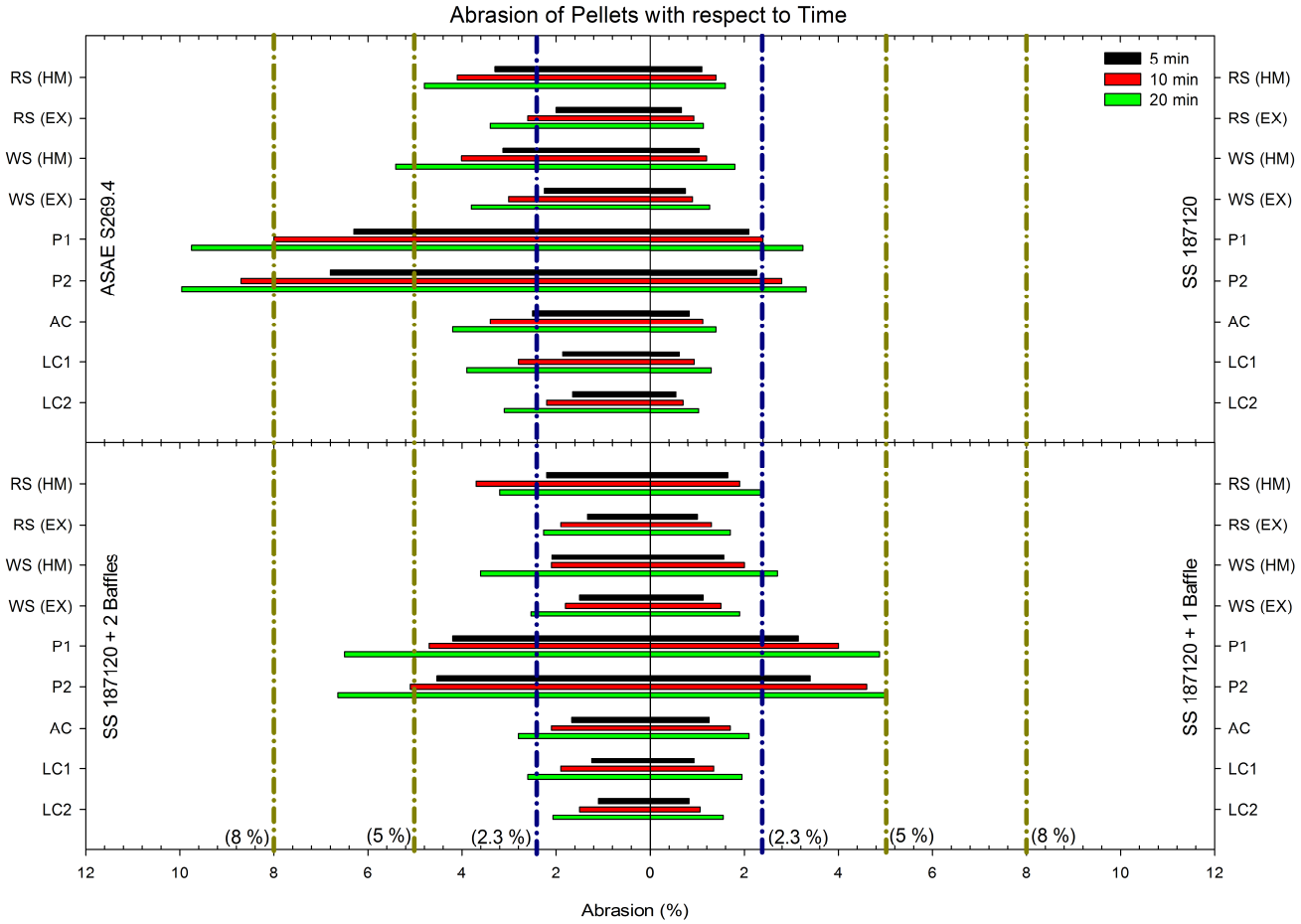


Figure 42: Abrasion of the straw pellets and their blends measured with two different tumbling devices (ASAE S269.4 and SS 187120) and the modifications of SS 187120 with one and two baffles.

The results obtained show a correlation between the two different abrasion standards (ASAE S 269.4 and SS 187120). Similar abrasion result trends are observed from both the tumbling devices. The increase in number of baffles in the SS 187120 increases the abrasion values of the pellets. The lower abrasion values from different standards with their modifications are plotted with the increasing abrasion values in figure 43.

The regression lines of the abrasion values obtained from SS 187120 show a tendency to reach the abrasion values obtained from ASAE S269.4 with increasing number of baffles. This is noted based on the increase in the abrasion values and increase in the angle of regression lines. The regression lines for P1 and P2 are drawn separately as these pellet blends result in higher abrasion values. The high abrasion values with the biogenous additives (palmitin and paraffin) are due to the increased brittleness of pellets.

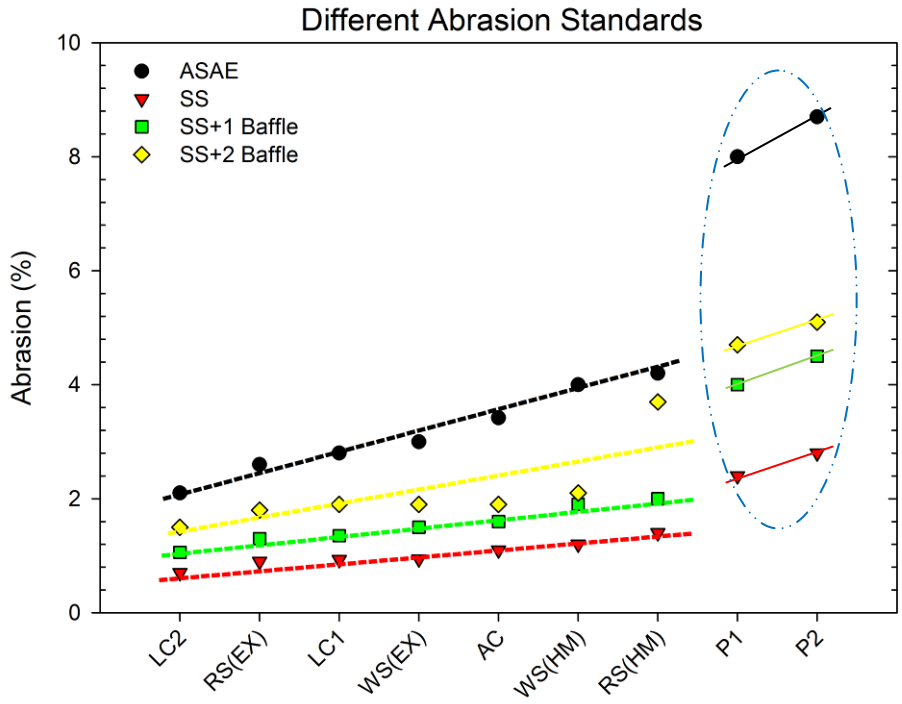


Figure 43: Comparison of abrasion values (tumbling time of 10 min) from different tumbling devices plotted with increasing abrasion values.

The results show a very good co-relation between the two durability testing devices. The co-relation also shows that the design and the installed baffles in the durability testing device have a significant influence on the results of the durability. Durability tester with a higher sphericity produce lower attrition as the pellets slide or roll around the walls of the durability testing devices, the numbers of direct encounters with the walls of the device are not as high as in the rectangular shaped device. Further it is also noticed that the installation of baffles increases the attrition due to the increasing number of impacts inside the rotating tumbling crates.

For the evaluation of strength, the maximum pressure force which a pellet can withstand is analysed. Pellets need to withstand different pressure forces as they are confronted with such pressures during handling, storage and transportation.

The results show that maximum pressure which a pellet can withstand is obtained from the pellets prepared with the water content of 17 wt. % (rye straw, P1, P2, and AC) and 18 wt. % (wheat straw, LC1 and LC2) (figure 44) corresponding to the lower abrasion values (figures 41).

The highest pressure which a pellet can withstand in the blends prepared is obtained with 34.2 wt. % lignite coal (LC1). The highest pressure which a rye straw pellet could withstand is 543 N and is recorded with the pellets prepared at 17 wt. % water content. With the implementation of the blend mixtures it is observed that there is an increase in pressure which the pellets can withstand. This increase in pellet pressure resistance reveals a significant correlation with the density and abrasion of the pellets blends.

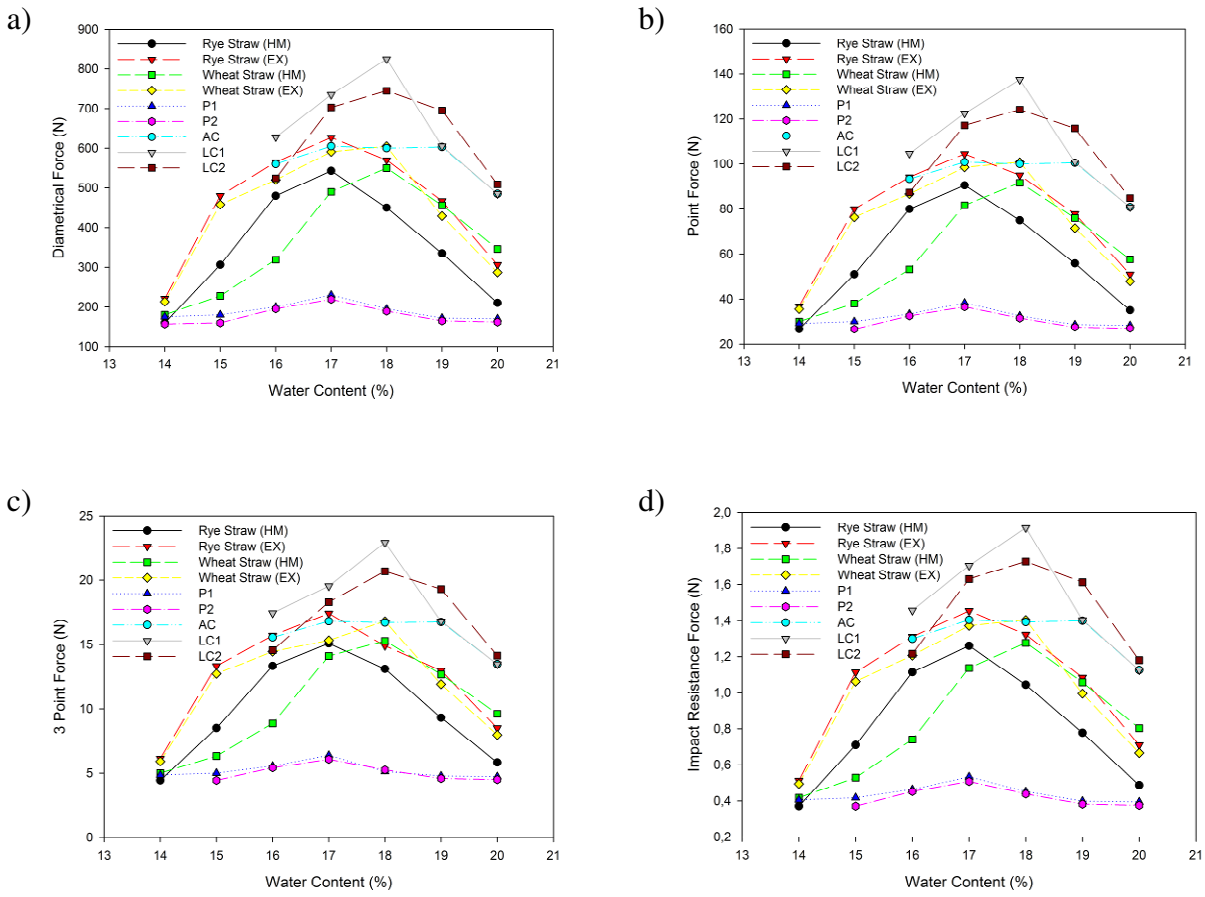


Figure 44: The strength of the pellets as measured using four different strength testing methods (diametrical force (a), point force (b), three point force (c) and impact resistance (d)).

Different correlations between strength parameters and durability /abrasion are displayed in figure 45. It is expected that there will be a decrease in strength of the pellets with increasing abrasion. The results show that there is a decrease in the diametrical force (figure 45a), three point force (figure 45c), point force (figure 45b) and impact resistance (figure 45d) force of the pellets with increasing abrasion values (positive correlation). This positive correlation can be related to the direction principle of forces acting on the pellets during various strength tests in comparison to the forces acting in abrasion testing devices.

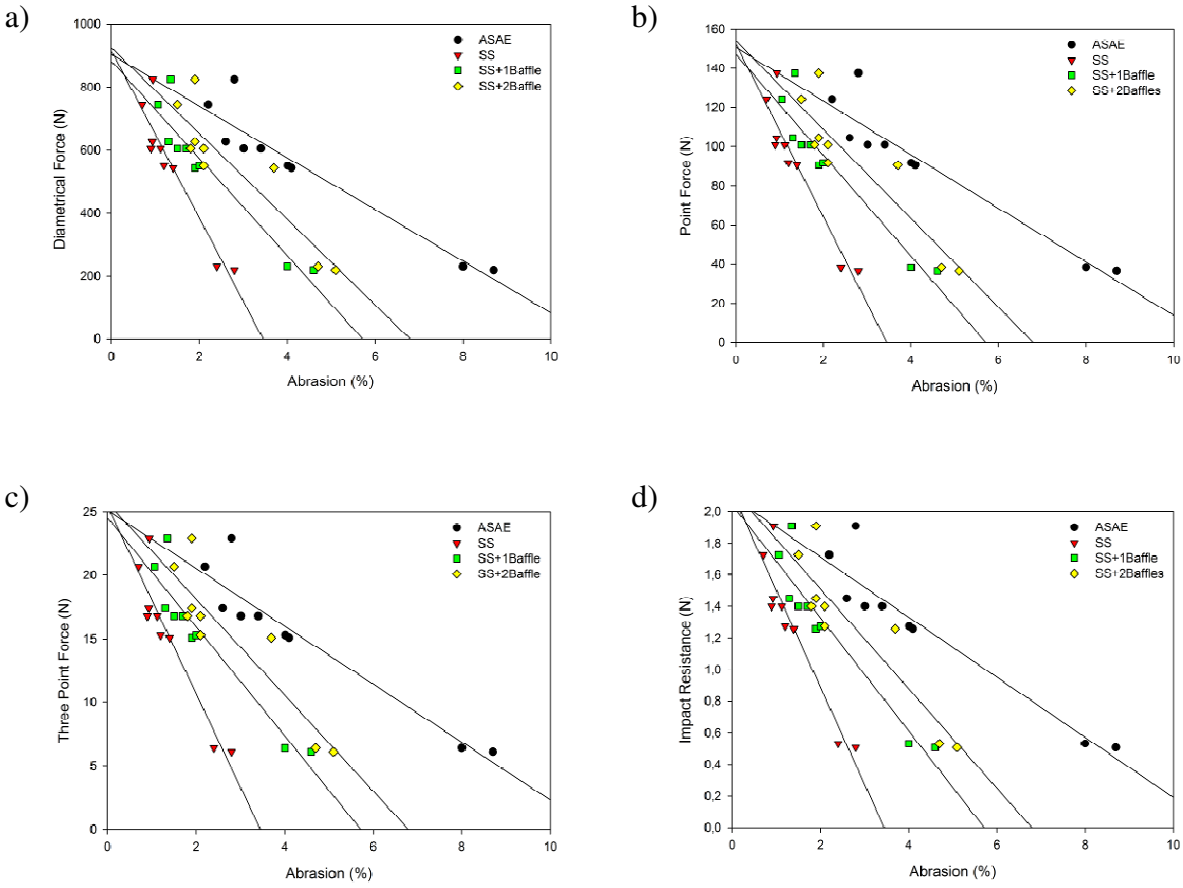


Figure 45: Different correlations between different strength parameters and abrasion as per ASAE S269.4 and SS 187120 of the cereal straw pellets and their blends.

4. Industrial residues: Black liquors (lignin) (publications 4 to 6)

This chapter deals with the production of granules / briquettes from different black liquors and discusses the conventional and innovative lignin separation processes from black liquors. The respective granules are produced with the help of build-up granulation processes using a spray-granulator, subsequently acidifying the produced granules and producing hydrophobic granules / briquettes. Further this chapter also tries to enlighten on the utilization possibilities of the produced end-products

4.1 Processing of black liquors from pulp and paper industries

Technical lignins (black liquors) from the sulphite as well as the sulphate pulp cooking process are selected for the investigations in this work. Calcium lignin sulphonate (Ca-LS) and sodium lignin sulphonate (Na-LS) from the sulphite process, Kraft lignin (KL) from the sulphate process are chosen as the main technical lignins in this thesis work as they are produced at industrial scales and are available in huge amounts. Calcium lignin sulphonate is produced from the calcium-bisulphite pulping process and sodium lignin sulphonate is produced from the neutral-sulphite pulping process (see chapter 2). The physical and chemical properties of these liquors are given in table 9.

The moisture content is determined using ASAE standard S269.4 where oven drying of the samples is carried out at 105 °C for 24 h.

Acidification is the process in which materials are treated with different acids. In case of black liquors acidification is used to precipitate lignin conventionally by making the dissolved lignin particles as non-soluble particles either through chemical reaction or by reducing the pH value. The insoluble lignin particles after acid treatment are developed due to the re-modification of structure, change in pH, change in particle charge, etc. The developed particles are mostly of fine dust / colloidal particle sizes (one nano meter to one micro meter). This process is mainly influenced by the type and concentrations of the acids. Acidification of calcium lignin sulphonate is carried out with H_2SO_4 (96 % conc.), acting as an example of the conventionally applied process in separating lignin from black liquor.

The black liquor is acidified by means of concentrated sulfuric acid, wherein the lignin sulphonate precipitates and is then separated using a filter basket centrifuge from the resulting suspension. Investigations are carried out with different amounts of acid giving a relationship between yield of lignin and amount of acid requirement. Further the influence of liquor temperature on the lignin yield is investigated. For this purpose, acidification is carried out at four different liquor temperatures (20 °C, 50 °C, 70 °C and 100 °C).

A basket centrifuge is used to separate lignin after acidification. The separated lignin is then dried and weighed to measure the amount of lignin yield. The lignin yield is calculated as a percentage of the total amount of lignin in calcium lignin-sulphonate black liquor.

Table 9: Physical and chemical characteristics of black liquors from sulphite and sulphate pulp cooking processes.

Characteristics	Sulphite		Sulphate
	Ca – LS	Na – LS	Kraft
Colour	Dark brown to black	Dark brown to black	Dark brown to black
Moisture content (%)	80*, 50**	55	75
pH	4.5	8.0	13.0
Density (kg m^{-3}) @ 20 °C	1240	1220	1020
Solubility	Soluble	Soluble	Soluble
Viscosity (mPa s) @ 20 °C	1000	200	
Sulphur (%)	6.93	7.59	7.35
Chlorine (%)	< 0.1	< 0.1	< 0.05
Calcium (%)	5	--	--
Sodium (%)	--	8	5 – 15
Alkaline Na_2O (%)	< 1	< 12	< 15
Invert sugar (%)	6	6	6 – 10

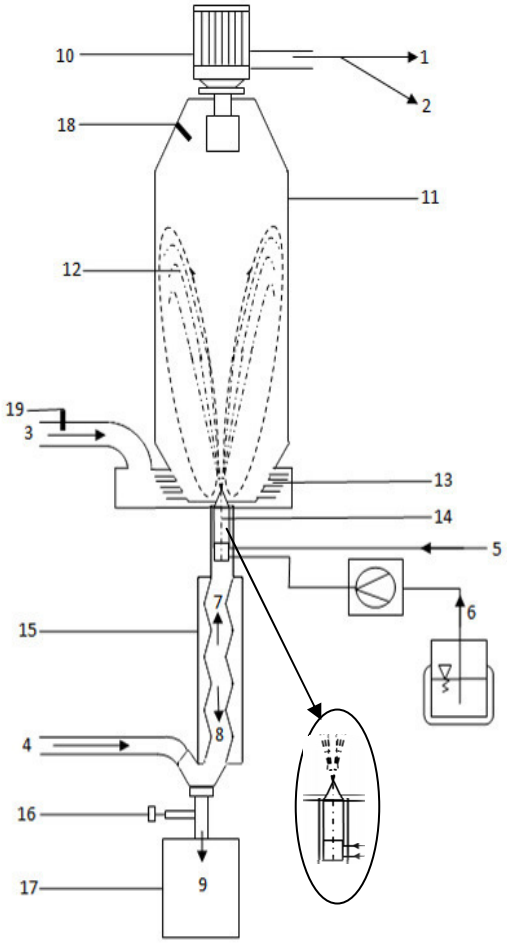
*acidification, **granulation

Technical lignins are subject to drying with varying temperatures (60 °C, 80 °C and 100 °C) with the help of an oven to understand the thermal behavior of lignin sludge's. The samples after drying at different temperatures are investigated for the development of pores under Leica-Microscope MZ8 (see chapter 3). This is carried out to determine the appropriate reactor temperatures of the spray-granulator in producing granules with specific required characteristics (porosity, strength, structure, etc.). Further the microscope is also used to determine particle size distribution of dried lignin powder.

The particle size distribution of the produced granules is carried out using a dynamic image analysis with the help of Camsizer from Retsch Technologies (see chapter 3). The assessment of particle size distribution is carried out with three representative samples for each variant (Ca-LS, Na-LS and KL); each sample on average has a minimum of 15000 particles.

Granulation / build-up pelletisation of the technical lignins is carried out with the help of a spray drier / spray granulator (type: 100 FSG from the company Alpine). The spray granulator is illustrated in figure 46. Lignins are pumped into the reactor with the help of a pump (6) through the two-stuff (material and air) nozzle (14). The evaporation process starts as soon as the material exits the nozzle. The material is made to circulate (12) in the reactor vertically due to the conical shape at bottom together with the air stream input. The material is made to circulate horizontally with the help of an air classifier (10) on top of the reactor. The classifier on top filters the accumulated dust particles, serving as a control in the development of granules with certain diameters. The granules build-up themselves into coarse granules with a certain weight, which then fall down into the collecting container (9, 17) passing through a zigzag de-dusting chamber (15). The zigzag de-dusting chamber prevents the falling down of low weight granules or dust particles (Heinrich, 2001; Heinze, 2000; Furchner and Schwechten, 1989). The goal is to produce granules having particle sizes greater than 100 µm to avoid explosion risks (Eckhoff, 2003).

The possibility to predefine different process parameters enables a wide production range of lignin granules. Spray granulation of calcium lignin sulphonate is carried out with increasing temperatures from 80 °C to 180 °C with an interval of 20 °C. Spray granulation of sodium lignin sulphonate is only carried out with temperatures of 80 °C and 100 °C based on the results obtained from calcium lignin sulphonate granules, and for the Kraft lignin at 100 °C due to high moisture content present in Kraft lignin liquor. The material input temperature is about 20 °C.



1 Air exiting the system
2 Dust removal
3 Hot air streaming into reactor
4 De-dusting through air pressure
5 Sprayer air stream
6 Material feeding
7 Fines
8 Granules
9 Continuous product discharge
10 Air separator for dust
11 Cylindrical Granules container
12 Circulating material
13 Conical ground air flow
14 Sprayer (material and air)
15 Zigzag deduster
16 Product discharge valve
17 Container for granules
18 Air exiting Temperature measurement
19 Input air Temperature measurement

Figure 46: Spray-granulator.

The strength indicates the quality of granules / briquettes and defines as the rate of force necessary to crush them. The strength tests for granules are carried out with the help of an automatic granule strength testing machine (GFP-Automatic) from the company Etewe GmbH (figure 47a), whereas the strength tests for briquettes are carried out with the ZWICK-ROELL (type: ZMART.PRO) material testing machine (figure 47b). The diametrical strength tests are carried out as these pressures occur during handling, transportation and storage of granules /briquettes (see chapter 2 and chapter 3).

Granules density is measured as the ratio of mass of granules in a cylindrical vessel to its predefined volume of 56.15 l as per standard ASAE S269.4, whereas the density of briquettes is measured individually by noting the dimensions and weight of respective briquettes. The elementary analysis of the raw technical lignins as well as of the granules / briquettes produced with spray granulation and after acidification are analyzed using the Elementar Vario MACRO CUBE.

a)

b)

Figure 47: (a) GFP Automatic from Etewe GmbH for measuring the granule strength and material testing machine (b) ZWICK-ROELL (type: ZMART. PRO) for testing the pellet /briquette strength.

The granules from Ca-LS, Na-LS and Kraft lignin liquors are produced with reactor temperatures of 80 °C and 100 °C. The produced granules are treated with different concentrations (70 %, 80 % and 90 %) of acids (H_2SO_4 / CH_3COOH) at varying temperatures (100 °C and 130 °C) for 15 minutes. The detailed schematic process (figure 48) in production of hydrophobic granules with the help of acid treatment is applied for patent (Narra et al., 2012; patent application number – 10 2010 102 327.1). The granules after the acid treatment are treated with warm water (80 °C) removing the acids adherent on the surface as well as inside of the acid filtered granules. The washing of granules with warm water is carried out till the pH value of the filtrate stabilizes. The acid treatment and washing process produces colloids (fine dust size particles) which are ending up in the filtrates. The filtrates obtained from the filtration of granules and after the washing of granules are sent to the regeneration unit, where the acids and water are regenerated and recirculated back into the process. The regeneration unit simultaneously separates colloids / fine dust size particles, which are sent to the raw black liquors increasing the solid matter content. Regeneration and recirculation escalates the efficiency of whole process by increasing the solid matter contents of black liquors.

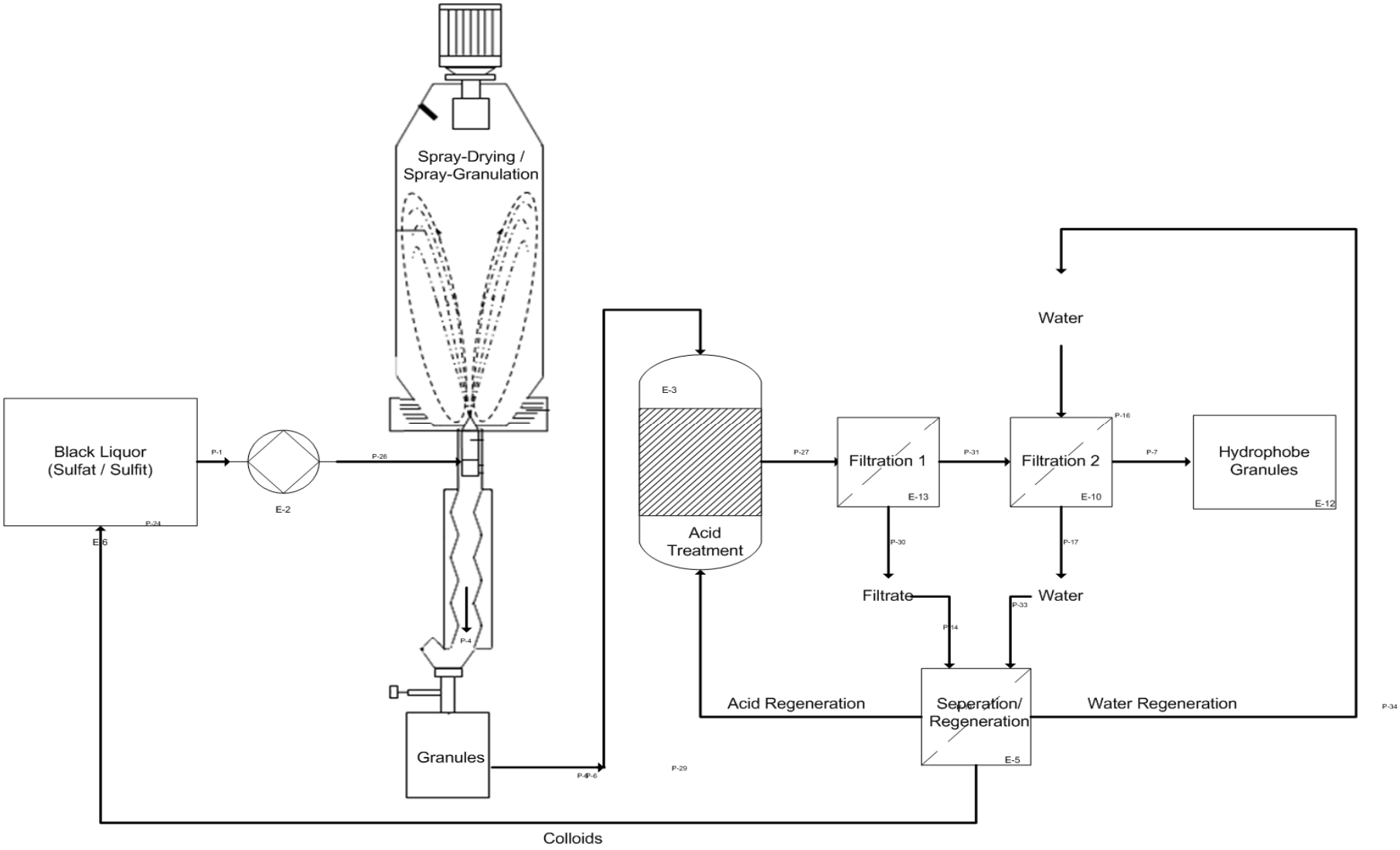


Figure 48: Schematic process in the production of hydrophobic granules (Narra et al., 2012; patent 102010102327.1).

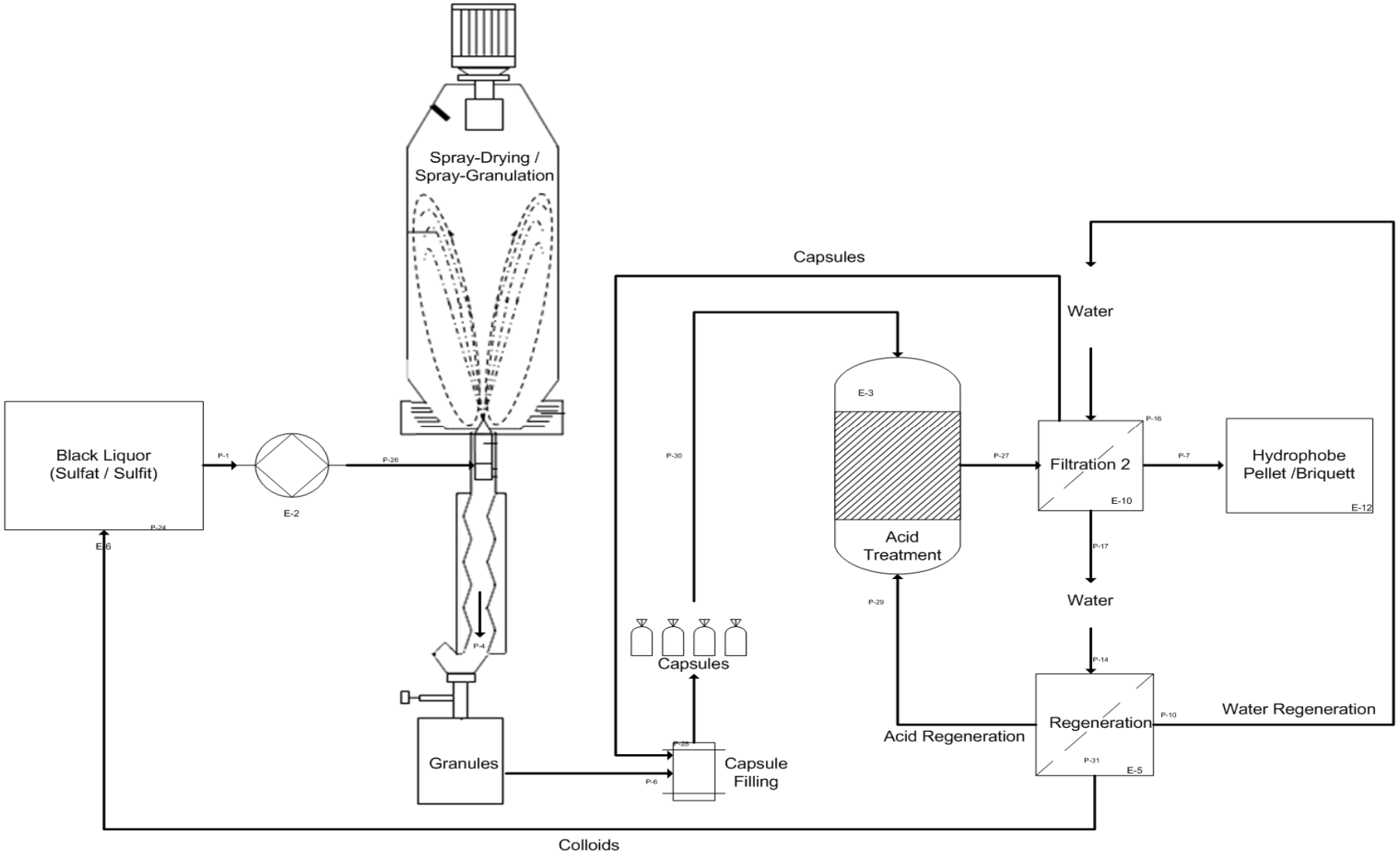


Figure 49: Schematic process in the production of hydrophobic briquettes using capsules (Narra et al., 2012; patent 102010102327.1).

The development of hydrophobic briquettes is achieved by filling the granules in a defined geometrical form (cylindrical capsule) having dimensions of 50 mm diameter and 60 mm height and treating them with the acids. The detailed schematic process (figure 49) in production of hydrophobic briquettes is applied for patent (Narra et al., 2012; patent application number – 10 2010 102 327.1). The treatment with the acids and the washing process are similar to that of the production process of hydrophobic granules. The advantages of the capsules utilization is that they can be utilized a higher number of times and at the same time reduces the first filtration unit in comparison to the hydrophobic granules production process. Further the production of briquettes in the acid treatment process reduces the percentage of colloids drastically, making the process more economic and efficient.

The water (liquid) holding capacity of the granules is tested by immersing the predetermined amount of granules in a beaker of glass filled with water. The granules are filtered with a sieve having an aperture size of 50 µm such that only excess water is allowed to flow through. The water content of the part of granules is measured and the remaining part of granules left to air dry.

4.2 Results and discussions based on the processing of black liquors

The water contents of lignin sulphonates are ranging from 50 to 55 wt. %, whereas Kraft lignin has a moisture content of 75 wt. %. The water content of the produced granules is ranging from 4 wt. % to 11 wt. % and the water content of end granules after the acid treatment, consecutive water washing steps and air drying is ranging from 5 wt. % to 10 wt. % after stabilization. The water content of the granules is either lower than or equal to that of the specified values (≤ 10 %) as per solid fuel standards. The water content has an influence on the net calorific value, combustion efficiency and the temperature of combustion (Nussbaumer and Kaltschmidt, 2001; Obernberger and Thek, 2002). The 10 wt. % water content results in high combustion efficiencies through which a high energy efficiency can be achieved (Kaliyan and Morey, 2006; Mani et al., 2006; Obernberger and Thek, 2004; Shaw and Tabil, 2007).

Acidification results of the calcium lignin sulphonate with respect to different liquor temperatures and concentration of acids are displayed in figure 50. It is found that both liquor temperature and concentration of acids have an influence on the yield of lignin precipitated and filtered. The highest lignin yield of about 58 % is obtained with a liquor temperature of 50 °C with 0.03 ml ml^{-1} concentration of sulphuric acid. There is no increase in yield observed with further increase in temperatures (70 °C and 100 °C). The increasing acid concentration (up to 0.035 ml ml^{-1}) results in increasing yield. Further increases in acid concentration resulted in a slight increase in yield of lignin but are not significant.

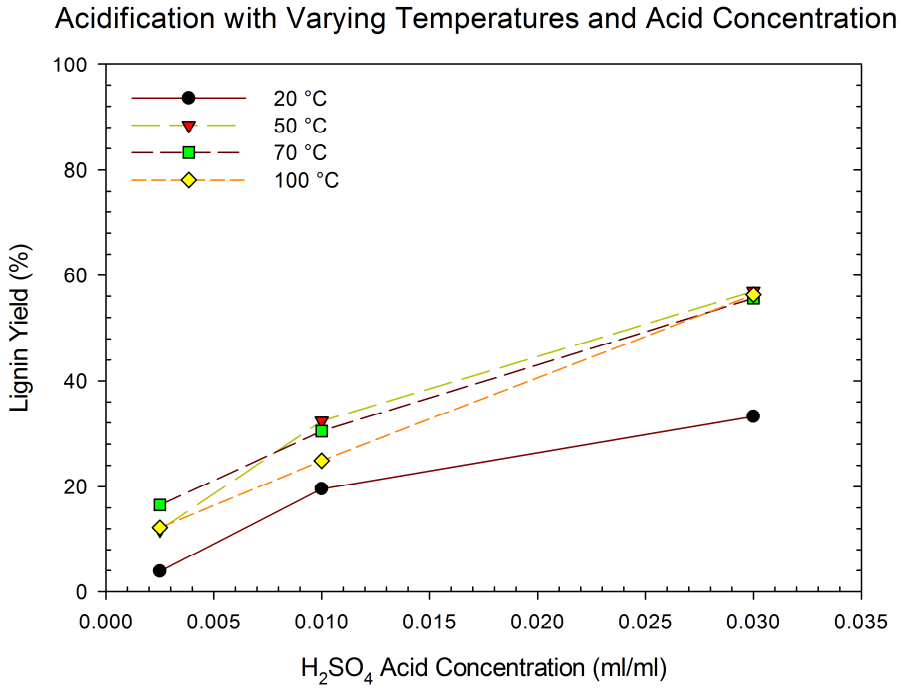


Figure 50: Lignin yield after separating with the help of a basket-centrifuge with respect to varying liquor temperatures and acid concentrations.

The elementary analyses of separated lignins are carried out with an acid concentration of 0.03 ml ml^{-1} and are given in table 10. The results show a tremendous increase in total sulfur (S) content from 6.93 % to about 29 %. Reasons for this may be the adhesion of sulfuric acid in the filter cake of the separated lignin as lignin sulphonate molecules have large adsorption capacities. In the conventional separation processes, this filter cake is washed with water removing the acid adherence and washing out the salts. The filtrate (spent / wash liquor) is sent back to the black liquor after the evaporation process. The ash content of the separated lignin also ranges from 27 % to 52 % (table 10), which is extremely high indicating a high content of calcium salts. An increase in the ash content is observed with increasing temperatures till 70 °C and thereafter a slight reduction in ash content is observed at 100 °C.

Table 10: Elemental analyses (free of water and ash) of the separated lignins through acidification of calcium lignin sulphonate with varying liquor temperatures at acid concentration of 0.03 ml ml^{-1}.

Temp	Moisture [%]	Carbon [%]	Hydrogen [%]	Oxygen [%]	Nitrogen [%]	Sulphur [%]	Ash [%]
Calcium Ligninsulphonate Liquor							
	50	56.37	5.41	31.07	0.22	6.93	13.49
Separated Lignin after Acidification							
20 °C	26.5	58.74	3.55	11.43	0.19	26.08	27.18
50 °C	24.93	58.28	3.77	8.41	0.19	29.30	43.79
70 °C	23.25	57.93	3.62	27.12	0.25	11.08	52.48
100 °C	23.35	58.80	3.60	20.15	0.22	17.30	49.76

The drying of lignin sulphonates (Ca-LS and Na-LS) and Kraft lignin at different temperatures (60 °C, 80 °C and 100 °C) over 24 h in an oven displays a clear thermal behavioral characteristic of the black liquor materials (figure 51). The dried material samples are analyzed for the development of pores and their sizes with respect to varying temperatures.

The average pores sizes measured for Ca-LS are 85 µm for 60 °C, 165 µm for 80 °C and 615 µm at 100 °C drying temperatures. The pore sizes of Na-LS and KL increased from 6 µm to 105 µm and from 8 µm to 109 µm respectively. The samples show an exponential increase in the pore sizes with increasing temperatures. The reason for this increasing pore sizes is due to the high dynamic viscosity (changing with temperatures) of the black liquors leading to the development of a foamy structure. The development of the foamy structure increases with increasing temperatures leading to the development of larger pore sizes. The low foamy structure development of the samples results in a bottom layer, which let the samples to deform plastically without leaving any fissures / cracks behind.

The spray granulation of lignin sludge's at high temperatures would result in granules having higher diameters compared to that of the granules produced at low temperatures. To investigate the transmissibility of the lignin sludge's influence on drying temperatures and pore sizes recorded from microscope to the spray granulator, granules from calcium lignin sulphonates are produced with varying temperatures ranging from 80 °C to 180 °C with a 20 °C interval (figure 52a). The sodium lignin sulphonate granules are only produced with reactor temperatures of 80 °C and 100 °C based on the results obtained from calcium lignin sulphonate granules. Granules from the Kraft lignin (figure 52a) are only produced at a temperature of 100 °C due to the high moisture content (75 wt. %) present in the Kraft lignin liquor. The granulations below 100 °C lead into adhesion of Kraft lignin liquor on the walls of the reactor.

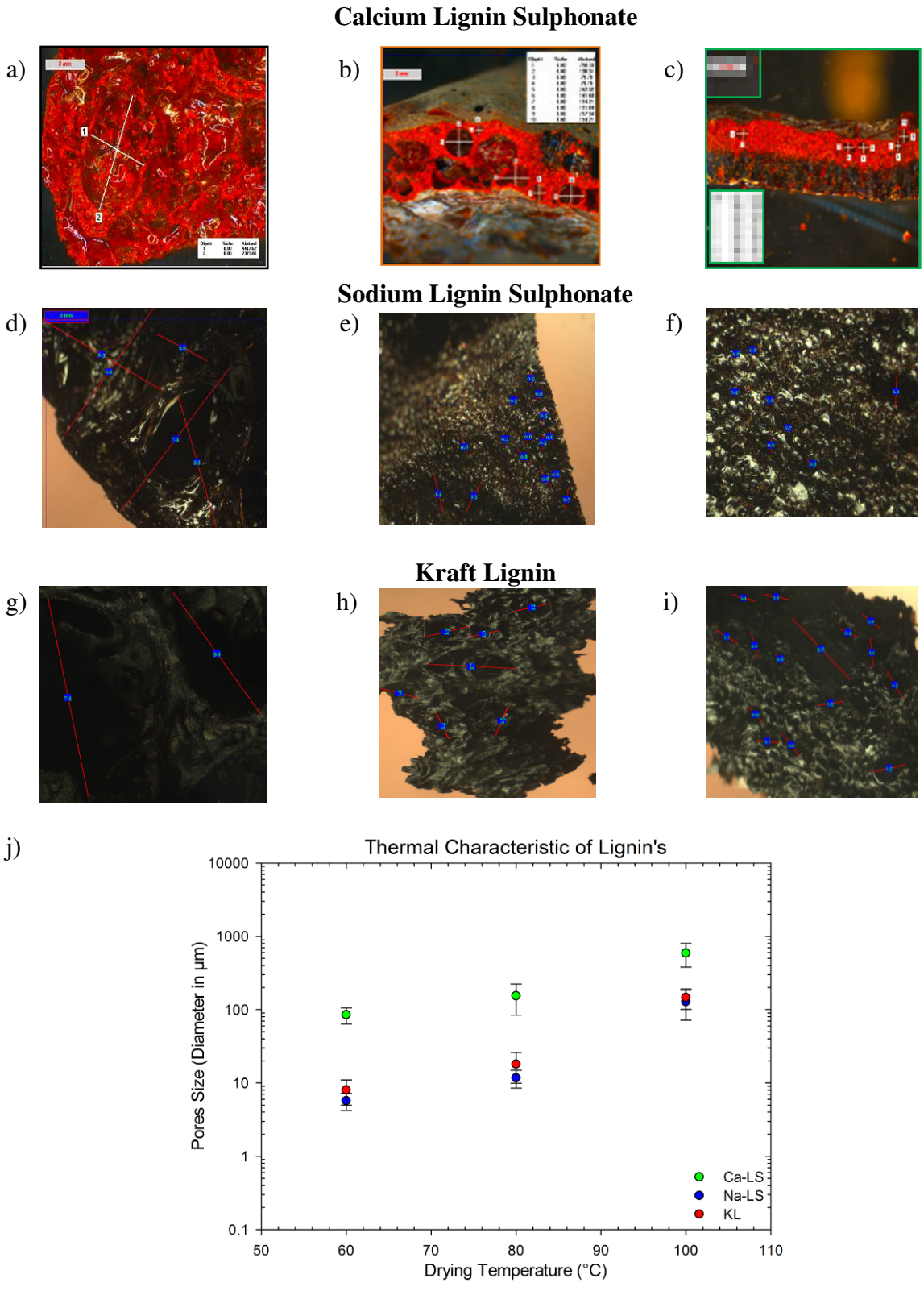


Figure 51: Thermal behavior of Ca-LS (a, b, c), Na-LS (d, e, f) and KL (g, h, i) with respect to varying temperatures of 100 °C (a, d, g), 80 °C (b, e, h), 60 °C (c, f, i) and the measured average pore sizes (j) with standard deviations.

The transmissibility of the results from the drying temperatures and pore sizes recorded from microscope to spray granulation is clearly observed with respect to the structure, colour, particle size and density of the produced granules. The granules produced at higher temperatures (> 100 °C) result in highly porous, low density, bigger particle size and are light brown in colour (figure 52c). The granules produced at lower temperatures (< 100 °C) result in high density, smaller particle size and are dark brown in colour (figure 52b). These characteristics of the produced granules with varying temperatures are due to the difference in the liquid evaporation inside the spray granulator. The produced granules are further analyzed with the microscope to determine the structure, colour, etc.

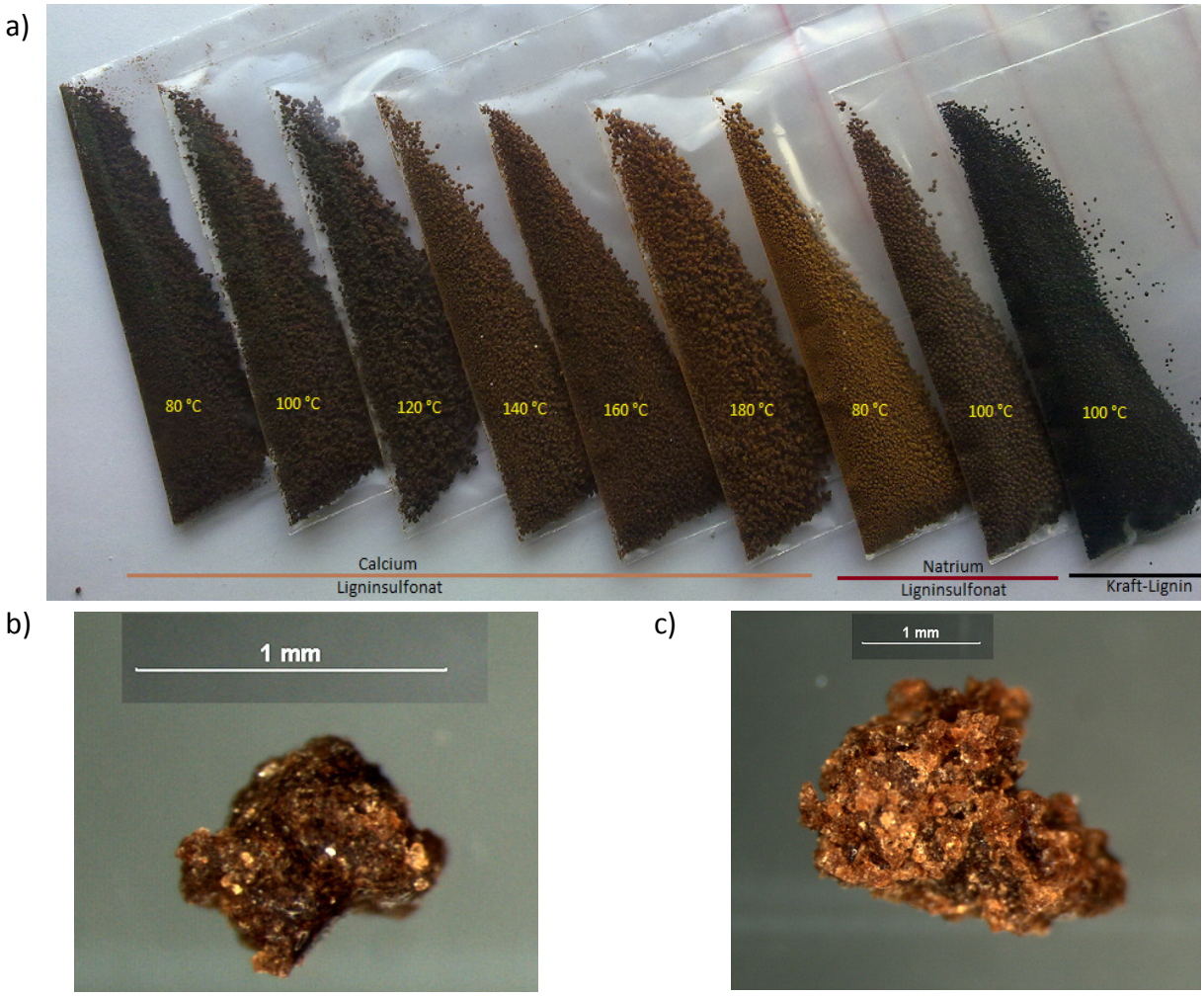


Figure 52: The granules produced from spray-granulation (a) with varying reactor temperatures from 80 °C till 180 °C with an interval of 20 °C for Ca-LS, 80 °C and 100 °C for Na-LS, 100 °C for KL. Structural analysis of the granules produced at (b) 80 °C and (c) 180 °C observed under microscope.

The produced granules are build-up by spraying the droplets into the reactor. The development of droplets into granules is based on the liquid evaporation from the droplets at different temperatures. The granules produced below 100 °C are almost round, whereas the granules produced at higher temperatures have irregular sizes and shapes due to the foamy expansion of the lignin sludge's. The colour difference of the granules (below 100 °C and above 100 °C) is due to the reason that the granules produced below 100 °C have not undergone complete liquid evaporation and the drying process only takes place over the surface.

The presence of liquid inside the developed granules let them fall through the zigzag de-dusting chamber due to the self-weight of the granule. The granules produced below 100 °C result in an increase in the strength of granules due to binding of dried particles on the surface with liquid kernel inside. The air drying of the granules produced above 100 °C does not show any increase in strength but have produced more dust particles in storage and transportation processes due to the disintegration of coherent particles lacking proper bonding.

The particle size distribution curves of different granules from different lignin sludge's with varying temperatures are depicted in figure 53. The particle sizes and their ranges are classified as dust (1 to 200 µm), dust explosion (10 to 100 µm) and dust free granules. The particle size distribution of lignin powder lies up to 95 % in the dust zone and 25 % to 88 % in the dust explosion zone, indicating a high risk of explosion. The granules lie slightly in the dust zone (< 3 %) and not in the dust explosion zone.

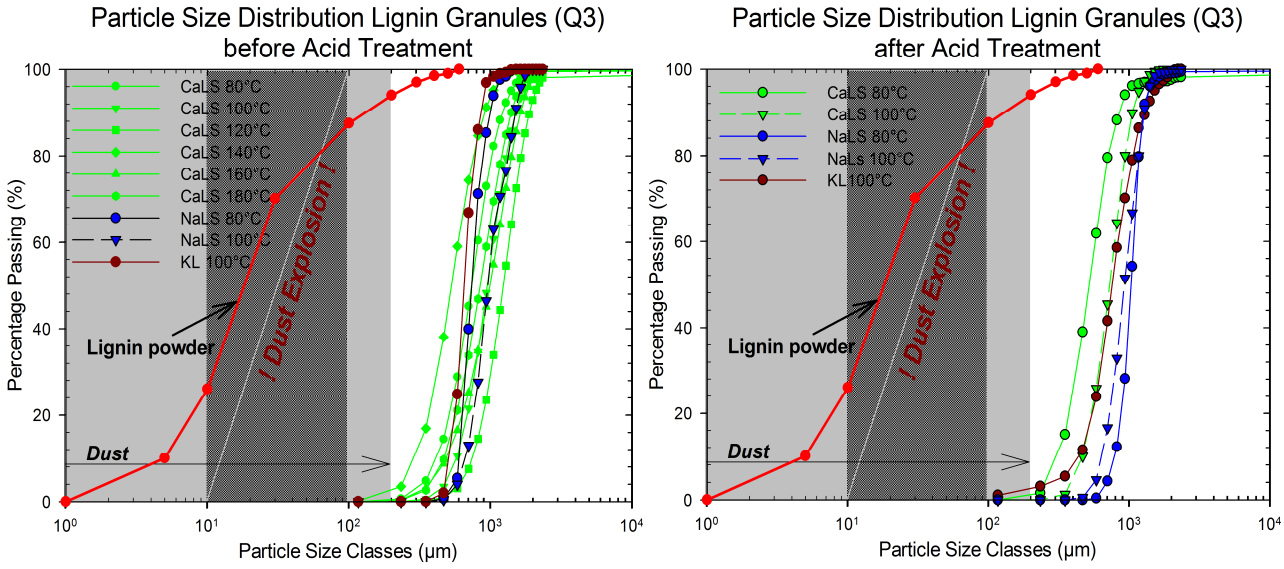


Figure 53: Particle size distribution of the dried lignin powder (red) and lignin sludge granules before (left) and after (right) acid treatment of i) calcium lignin sulphonate (Ca-LS: green), ii) sodium lignin sulphonate (Na-LS: blue) and iii) Kraft lignin (KL: dark red) with varying temperatures.

The fuel property which changes with the spray granulation / briquettisation of lignin sludge is the reduction of moisture content simultaneously producing dense agglomerates. The measured bulk density of the granules ranged from 490 kg m^{-3} to 670 kg m^{-3} (figure 54a). Dried lignin powder has a density of 600 kg m^{-3}. The density of granules measured is lower than the density of lignin powder produced at temperatures of 140 °C, 160 °C and 180 °C. The density of granules reduces with increasing temperatures. This reduction of density with increasing temperatures is due to the building up of foamy granule structures having high porosity at high temperatures. The high porosity and the foamy structured granules have high volume and low weight. High density of granules is important as this significantly reduces the storage, transportation, handling and fuel feeding costs and simultaneously increasing the energy density.

The evaluation of strength is carried out by analyzing the maximum pressure force which the granules can withstand (figure 54b). Granules need to withstand different pressure forces as they are confronted with such pressures during handling, storage, transportation and feeding. The withstanding pressure of the granules reduces with increasing reactor temperatures due to the development of foamy structured granules containing high amount of pores. The development of high amount of pores and their proportional increase with increasing temperatures results in reduction of density as well as the strength of produced granules.

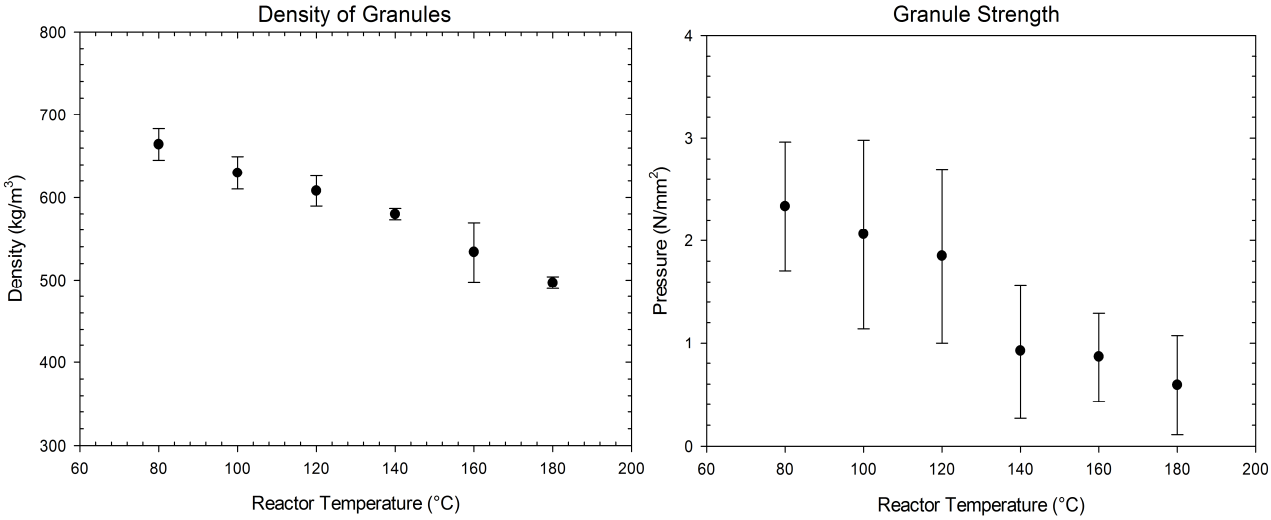


Figure 54: Bulk density (a) of the granules and their withstanding strength (b) measured with respect to the granulation temperature.

The granules produced with the spray granulator are hydrophilic (calcium- and sodium lignin sulphonates), hygroscopic (Kraft lignin) and contain impurities (cooking chemicals). The impurities are measured by means of the sulphur and ash contents in the granules. High sulphur and ash contents create problems in the combustion process such as high flue gases and slag formation.

The material utilization requires low sulphur contents for the development of environmental friendly products from lignin such as binders, compounds / composites (bio-plastics), etc. The removal of impurities from the granules is achieved by treating them with different concentrations of acids (H_2SO_4 / CH_3COOH) at different temperatures.

The treatment of granules with acids results in the change of solubility characteristics along with the removal of impurities. The granules after the acid treatment are hydrophobic. Lignin sludge granules from lignin sulphonates and Kraft lignin before (glass 1 and glass 2) and after (glass 3 and glass 4) the acid treatments are suspended in water to determine their solubility (figure 55). The acid treated granules do not show any water solubility in comparison to the untreated soluble granules.

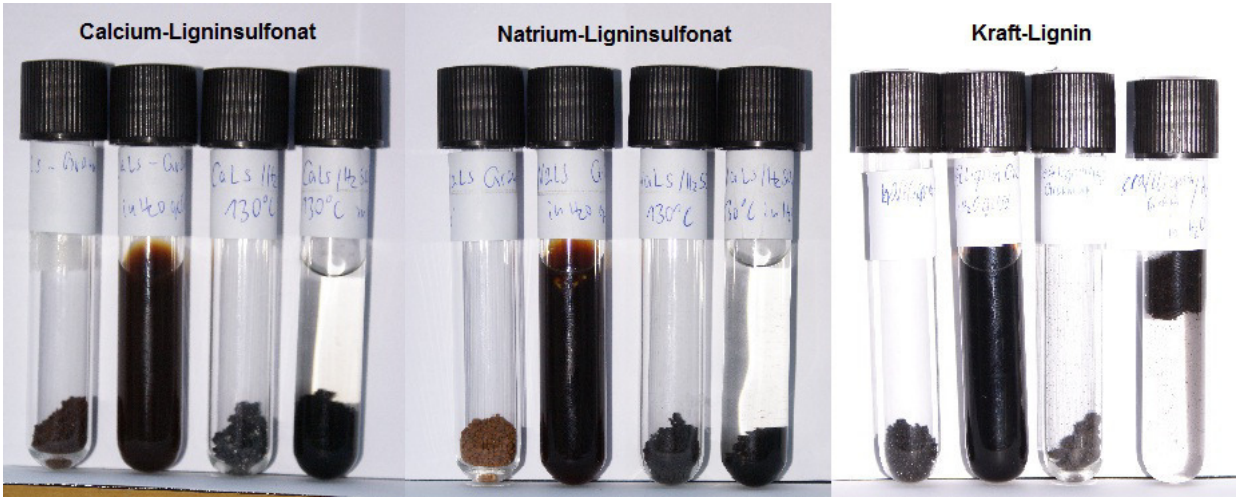


Figure 55: The solubility of lignin sludge granules after spray granulation (glass 1 and glass 2) and respective acid treatment (glass 3 and glass 4).

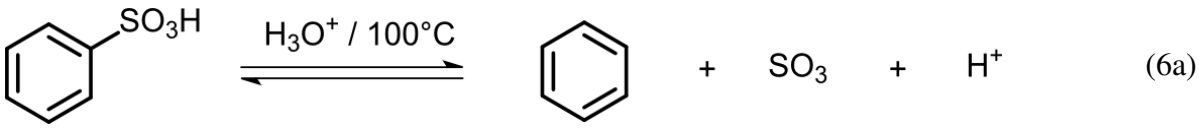
Lignin polymer before the pulp cooking process is insoluble in water, and is made soluble either by breaking (Kraft lignin) or modifying (lignin sulphonate) the structure of lignin with the help of cooking chemicals and high cooking temperatures. The treatment of granules with acids brings back the structure of lignin to its original form due to the re-modification of structure (insoluble in water). The re-modification of the lignin structure plays an important role in its storage stability.

The insoluble lignin granules are easier to store for longer times and do not develop into clumps in the presence of water (see chapter 1) due to their hydrophobic property. The insoluble / hydrophobic property of lignin granules also makes the warm water washing process more efficient and results in high yields of pure lignin.

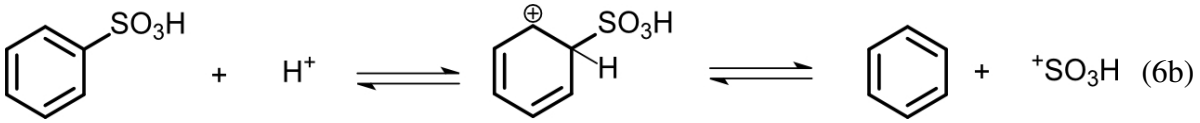
The treatment of granules with acids only modifies the reversible process (desulphonation) without any changes in granule size and shape. The granules offer high surface area for the reaction with acids and the reaction is more efficient compared to the acidification process in the liquid liquor with the same acids.

The acidification process is inefficient due to the losses through exothermic reaction of acids related to the high moisture contents in black liquors. The compact dense granules retain their structure avoiding / reducing the formation of colloids in the acid treatment process making the filtration, separation and washing processes easier and efficient.

The sulphite pulping process (lignin sulphonates) makes lignin soluble in water through the modification of its structure with the substitution of a reversible aromatic electrophil (HSO_3^-). The treatment of granules with H_2SO_4 is a desulphonation process (Zhu and Luo, 2007) making the reverse reaction with respect to the pulp cooking process and detaches the adherent sulphonate groups. The reactions occurring in the desulphonation process are given in equation 6a and equation 6b. The acid must be diluted to catch the released electrophil HSO_3^-, resulting in to water insoluble lignin sludge granules.



(6a)



(6b)

The sulphate pulping process (Kraft lignin) makes the lignin soluble by dissociating the phenolic hydroxyl (OH^-) groups in an alkaline medium. The acidification of Kraft lignin reducing the pH value from 13 to 11 would precipitate lignin. This process can be carried out either with acetic acid (CH_3COOH) or with sulphuric acid (H_2SO_4), through which lignin regains its water insoluble characteristic improving the purity (Liu et al., 2009; Ohman and Theliander, 2007) of granules.

A warm water (< 100 °C) washing of the granules (Ca-LS, Na-LS and KL) has to be carried out afterwards to remove the adherent acids from the granules after their treatment with acids. This process step is done till the pH value of the filtrate rises from 0.2 to 3. The elementary analysis of the lignin sludge's as well as the produced granules with different temperatures (80 °C and 100 °C) and the granules after the acid treatments (table 11) are analyzed to check the suitability of them for their different utilization purposes (material as well as energy applications).

The water and ash free heating values of the lignin sludge's as well as the granules before and after the acid treatments and for the briquettes formed during the acid treatment process are calculated based on equation 7 (Kaltschmitt et al., 2009) from the values obtained from elementary analysis.

The water and ash free heating values of the granules before and after the treatment remain the same (± 0.5 MJ kg^{-1}), also indicating no losses in energy efficiency.

$$H_O(waf)= 0.3491*X_C+1.1783*X_H+0.1005*X_S–0.0151*X_N–0.1034*X_O–0.0211*X_A \quad (7)$$

The impurities in the granules are measured with respect to their sulphur and ash contents. The sulphur and ash contents analyzed in the lignin sludge's are ranging in between 6.9 % to 7.6 % and 13.5 % to 44.4 % respectively. The sulphur and ash contents in calcium lignin sulphonates, sodium lignin sulphonates and Kraft lignin granules after spray granulation and before the acid treatment are having the same values as that of the lignin sludge's. This indicates that the spray-granulation process has only evaporated the water content present in black liquors. The calcium lignin sulphonate, sodium lignin sulphonate and Kraft lignin granules after the acid treatment show a high reduction in sulphur (from 6.93 % to 4.01 %, 7.59 % to 4.17 % and 7.35 % to 2.70 %) and ash contents (from 13.5 % to 3.9 %, 21.2 % to 0.58 % and 44.37 % to 0.58 %). This reduction in sulphur and ash contents is due to the washing of granules with warm water resulting in efficient cleaning of pores removing the salts, cooking chemicals and acids increasing purity of lignin granules. The sulphur and ash content of the granules after the acid treatment have significantly reduced indicating the removal of impurities with stabilization of the granule structure.

The granule structure makes the filtration process easier and efficient. The resulting granules have no explosion risk because of their low dust content based on their particle sizes (> 100 µm). The end product (hydrophobic granules) has low sulphur and low ash contents indicating the purity and high potential in material applications as well as energetic utilization. The resulting granules offer better handling, storage, and transportation of the produced end-product compared to black liquors or lignin powders and do not create any additional risks.

Table 11: Elemental analysis (water and ash free) of lignin sludge's spray-granules before and after the acid treatment.

Material	T_R /C /T_C [°C]	Moisture [%]	Carbon [%]	Hydrogen [%]	Oxygen [%]	Nitrogen [%]	Sulphur [%]	Ash [%]	H_O (waf)
Lignin sludge`s									
Calcium-LS	--	50	56,37	5,41	31,07	0,22	6,93	13,49	23,25
Sodium-LS	--	55	59,92	5,64	26,65	0,23	7,59	21,2	25,12
Kraftlignin	--	75	66,42	6,42	19,62	0,20	7,35	44,37	28,52
Calcium lignin sulphonate Granules									
Before Acid Treatment	80	8,65	56,27	5,41	31,30	0,22	6,80	13,52	23,17
	100	8,70	56,47	5,41	30,84	0,22	7,07	13,46	23,32
After Acid Treatment (H_2SO_4)	80 /70 /100	5,54	64,06	2,68	25,81	0,20	7,26	8,21	23,40
	80 /70 /130		65,81	4,73	24,60	0,20	4,66	8,01	26,30
	80 /80 /100		61,30	2,88	30,02	0,19	5,60	3,93	22,16
	80 /80 /130		62,73	0,35	32,65	0,26	4,01	4,52	19,23
	100 /70 /100		66,16	4,79	23,86	0,19	5,00	8,26	26,59
	100 /70 /130		66,95	2,71	25,85	0,25	4,23	6,70	24,17
	100 /80 /100		66,01	4,31	24,90	0,20	4,58	5,77	25,88
	100 /80 /130		64,62	3,76	26,61	0,39	4,63	5,88	24,57
Sodium lignin sulphonate Granules									
Before Acid Treatment	80	3,95	60,02	5,93	25,93	0,27	7,86	22,20	25,57
	100	8,99	59,81	5,34	27,36	0,18	7,31	20,20	24,64
After Acid Treatment (H_2SO_4)	80 /70 /100	8,56	63,76	3,93	25,85	0,20	6,26	2,48	24.79
	80 /70 /130		64,35	4,17	27,16	0,16	4,17	0,31	24.97
	80 /80 /100		61,73	4,10	27,58	0,21	6,37	1,18	24.14
	80 /80 /130		63,36	3,48	28,33	0,15	4,67	0,32	23.75
	100 /70 /100		62,45	4,60	26,54	0,19	6,22	3,89	25.01
	100 /70 /130		64,10	3,40	27,69	0,19	4,62	0,58	23,96
	100 /80 /100		62,77	4,00	26,77	0,20	6,26	1,61	24.45
	100 /80 /130		62,95	4,66	25,94	0,20	6,25	4,84	25.30
Kraft lignin Granules									
Before Acid Treatment	100	10,20	66,42	6,42	19,62	0,20	7,35	44,37	28,52
After Acid Treatment (H_2SO_4)	100 /70 /100	5,00	62,80	5,08	22,43	0,20	9,48	0,24	26.54
	100 /70 /130		63,99	5,07	22,07	0,22	8,65	0,58	26,88
	100 /80 /100		61,89	4,60	21,02	0,21	12,28	0,70	26,07
	100 /80 /130		57,98	4,60	24,47	0,20	12,73	0,25	24,41
(CH_3COOH)	100/50/21	7,65	71,65	5,49	19,95	0,21	2,70	0,51	33,19

The modification of the hydrophobic lignin granule production process with the help of a geometrically pre-defined volume constraint filtration capsule results in the formation of briquettes. The production of Kraft lignin briquette required application of additional pressures. The additional pressure is required to bind the low molecular weight Kraft lignin particles. The application of additional pressures was carried out after acid treatment directly inside the capsule. The produced briquettes are shown in figure 56. The formation of briquettes is due to the melting and bridging (solid-bridges) of granules.

Figure 56: The produced briquettes from Ca-LS (left), Na-LS (middle), and Kraft lignin (right) granules by treating them in filtration capsules with acids.

The briquettes have a higher energy density (due to compaction in the volume constraint capsule), better storage and handling properties than the granules. The elementary analyses of the produced briquettes are given in table 12. The briquettes produced from calcium lignin sulphonate and sodium lignin sulphonate result in higher sulphur and ash contents in comparison to the lignin sludge's and spray granules before acid treatment, this is due to the containment of acids, cooking chemicals and salts inside. Even though the briquette produced from Kraft lignin show a reduction in sulphur (from 7.35 % to 5.93 %) and ash contents (44.37 % to 41.30 %), they are not significant as they still contain impurities. A reduction in water and ash free heating value of the briquettes is observed in comparison to the granules. This reduction in heating values is due to the presence of high amounts of impurities. The high amount of impurities can be related to the inefficient washing process due to the enclosement of impurities inside where the warm water could not percolate to wash them.

The advantage of the new innovative and refinement processes are the obtainment of integrated agglomerates (granules / briquettes) in comparison to the conventionally carried processes. The conventional process requires an additional agglomeration process step in producing pellets after drying and comminution of the lignin cake.

Table 12: Elemental analysis (water and ash free) of briquettes produced in the acid treatment process.

Material	T_R /C /T_C [°C]	Moisture [%]	Carbon [%]	Hydrogen [%]	Oxygen [%]	Nitrogen [%]	Sulphur [%]	Ash [%]	H_O (waf)
Calcium-ligninsulphonate Briquettes									
After Acid Treatment	80 /80 /130	41.89	49.81	2.64	26.67	0.24	20.64	15.80	19.48
Sodium-ligninsulphonate Briquettes									
After Acid Treatment	80 /70 /130	18.4	51.76	4.31	28.39	0.16	15.37	18.48	21.37
Kraft-lignin Briquettes									
After Acid Treatment	Acetic acid (50 % C)	7.50	52,50	7.52	33.88	0.17	5.93	41.30	23.41

The strength of the produced hydrophobic granules / briquettes is further measured after the acid treatment and water washing process steps (figure 57). An increase in the strength (2.2 N mm^{-2} to 6.1 N mm^{-2}) of the calcium lignin sulphonate (Ca-LS) and sodium lignin sulphonate (Na-LS) granules after the acid treatment and water washing processes have been observed. However a decrease in the strength of Kraft lignin (KL) granules from 2.2 N mm^{-2} to 0.07 N mm^{-2} is observed. This respective increase and decrease of granule strengths can be directly related to the molecular weight (20000 g mol^{-1} to 143000 g mol^{-1} for lignin sulphonates and 2000 g mol^{-1} to 5000 g mol^{-1} for Kraft lignin) of the modified lignins in their respective liquors and their modified structures. The molecular weight of lignin in black liquors depends on the structure of modification, the type of the disintegration process as well as on the degree of delignification. Further the molecular weight of lignin influences the bonding of the single molecules through which the stability of the produced granules is affected. Due to the higher molecular weight more molecular bonding is assured in Ca-LS and Na-LS increasing the strength of the produced hydrophobic granules, whereas in KL a lower strength of the granules is observed which is due to the lower molecular bonding.

The briquettes produced from Ca-LS, Na-LS and KL show higher strength bearing capacity (breakage force in Newtons) (ranging about 900 N) compared to that of the granules before (0.69 N) and after acid treatment (1.8 N for lignin sulphonates and 0.02 N for Kraft lignin).

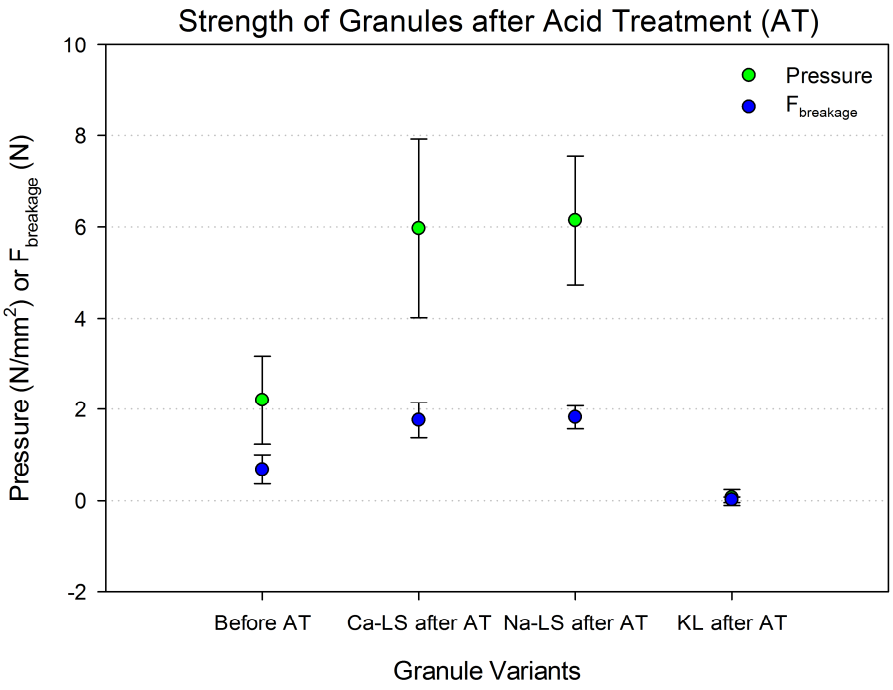


Figure 57: Strength of the acid treated granules measured with GFP automatic.

The **energy consumption** of the spray granulation process for the production of granules is composed of the base energy, evaporation energy and pumping energy required for running the spray granulator continuously. The energy consumption of the spray granulator is calculated by measuring the ampere and voltage values using equation 8. Lower energy (10 MJ h^{-1}) is required with lower reactor temperatures (60 °C) and increases linearly with increasing temperatures (figure 58a). The pump with minimum (0.95 l h^{-1}) and maximum (3.67 l h^{-1}) feeding rates of black liquor into the spray granulator requires an energy consumption of 0.05 MJ h^{-1} and 0.08 MJ h^{-1} respectively.

Joule = Ampere*Voltage*Time in seconds (8)

The energy consumption of the spray granulation process is also dependent on the ratio of amount of black liquor pumped into the reactor to that of the throughput of respective granules produced. The energy required with respect to the throughput is given in figure 58b. The energy consumption reduces exponentially with increasing throughput.

The throughput was calculated based on the specifications of the spray granulator used (FSG from the company Alpine), which states that it can produce maximum up to six kilograms of granules per hour from liquids having about 50 wt. % to 60 wt. % water contents. This is the main reason that the curves start with a throughput of six kilograms.

The blue line at 10 MJ h^{-1} (figure 58a) or 10 MJ kg^{-1} (figure 58b) is chosen as the acceptable energy requirement and is calculated with differences between the calorific values of black liquors in dry state (26 to 27 MJ kg^{-1}) and their energy losses due to evaporation (on average 10 MJ kg^{-1}) when they are incinerated directly (17 MJ kg^{-1}) (see chapter 1). The throughput of granules from the spray granulator has to be more than or equal to one kilogram per hour to obtain a positive energy balance depending on the reactor temperature (80 °C or 100 °C).

Further the acid treatment of granules / briquettes also require energy supply as they have to be treated at different temperatures. The energy consumption of the acid cooking reactor is around 0.5 MJ h^{-1}. The positive energy balance of the total process energy (feeding pump, spray granulator, acid cooking) requirement can only be achieved when the throughput of the granules from the spray granulator is more than or equal to that of two kilograms per hour. These values are calculated as per the literature values stating evaporation losses of 10 MJ kg^{-1}.

The positive energy balance is mainly dependent on the heating value of the end product along with their throughput. The heating values of various sulphite (Ca-LS, Na-LS) and sulphate (KL) pulped liquor granules calculated after acid treatment were approximately 26 MJ kg^{-1}, 25 MJ kg^{-1} and 33 MJ kg^{-1} (table 11), whereas the heating values of the produced briquettes are approximately 19 MJ kg^{-1}, 21 MJ kg^{-1} and 23 MJ kg^{-1} (table 12) respectively.

The heating values of the different black liquors were obtained graphically (figure 58c) based on the heating values of the granules and their influence with water contents (see chapter 2) as suggested by Nussbaumer and Kaltschmitt, (2001); FNR, (2007). The 50 wt. % of Ca-LS and 55 wt. % of Na-LS water contents in lignin sulphonates resulted in reduction of heating values from 26 MJ kg^{-1} to 11 MJ kg^{-1} (15 MJ kg^{-1}) and from 25 MJ kg^{-1} to 9 MJ kg^{-1} (16 MJ kg^{-1}) respectively. The 75 wt. % water content of Kraft lignin resulted in heating value reduction of 28.1 MJ kg^{-1} (from 33 MJ kg^{-1} to 4.9 MJ kg^{-1}).

Depending on the original black liquor moisture content (Ca-LS: 50 wt. %, Na-LS: 55 wt. % and KL: 75 wt. %) and the heating values (Ca-LS: 11 MJ kg^{-1}, Na-LS: 9 MJ kg^{-1} and KL: 4.9 MJ kg^{-1}) the reference blue line at 10 MJ h^{-1} or 10 MJ kg^{-1} in figure 61a and figure 61b shifts either to the left or to the right. This shifting of the blue line towards the right or left side is dependent on the difference of the heating values of the produced granules and the heating values of the black liquors. Ca-LS (blue dotted line), Na-LS (blue long dashed line) and KL (blue short dashed line) indicate a shift towards the right side as the differences in heating values are higher than that of 10 MJ kg^{-1} (figure 58b).

The shift of reference blue line to the right side signifies that the positive energy balance can be achieved with lower throughput than two kilograms. The throughput of the black liquor granules from spray granulator with respect to their blue line shift has to be either equal to or more than one kilogram for achieving a positive energy balance.

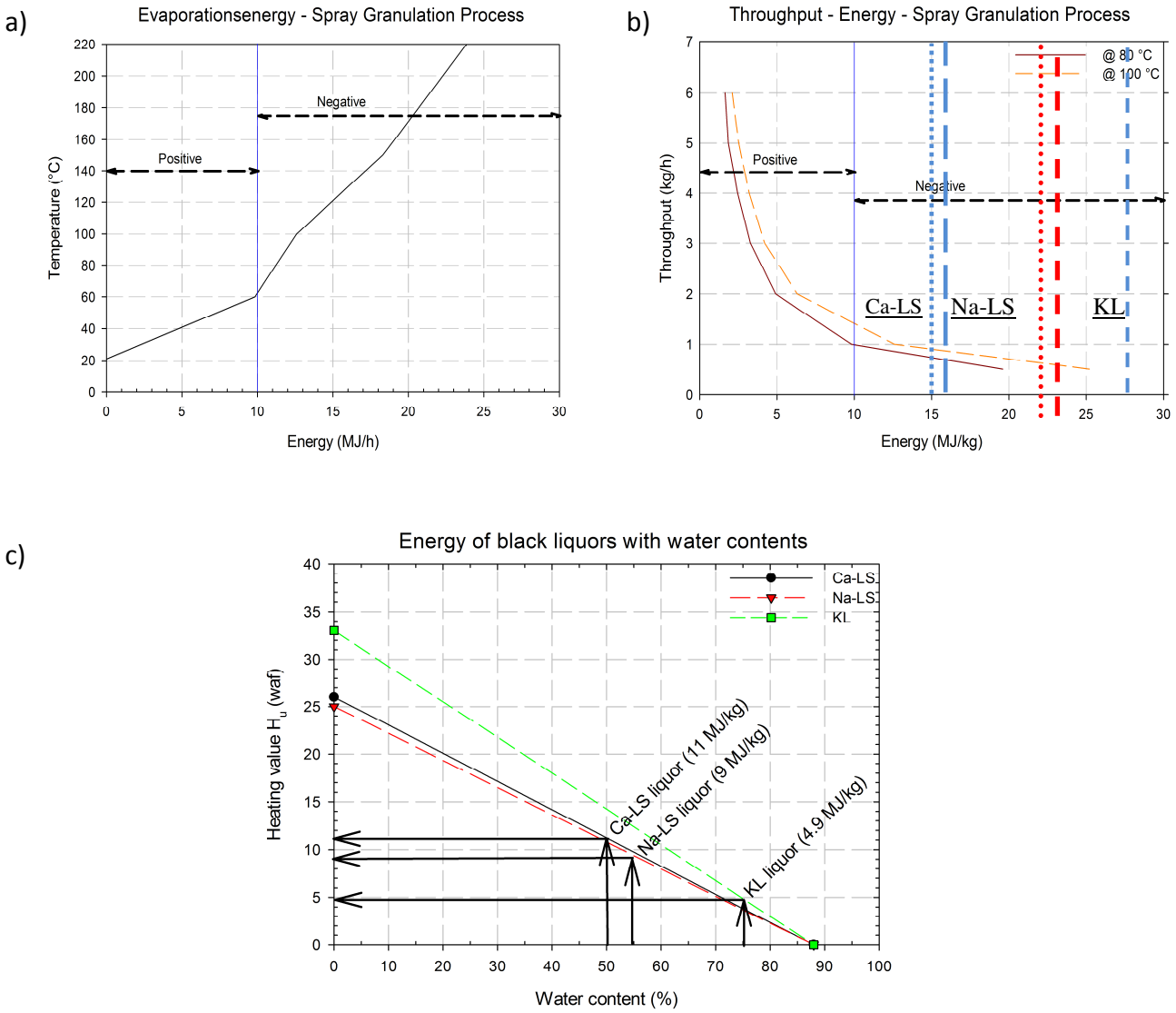


Figure 58: a) Evaporation energy, b) throughput energy of the lignin granules from the spray granulation process, and c) the graphically obtained heating values of the liquors when incinerated with their respective water contents (50 wt. % to 75 wt. %).

Further the energy requirement in building up of the granules in the spray granulator is calculated based on the evaporation energy requirement per each liter of moisture content (water content). Evaporation of one liter (one kilogram) of water requires 2.44 MJ of energy (FNR, 2007; Engineeringtoolbox.com, last visited on 25.10.2012). The spray granulation process evaporates water during the building up process of the granules. The differences in water contents per kilogram of the liquid black liquors (50 wt. % for Ca-LS, 55 wt. % for Na-LS and 75 wt. % for KL) and the black liquor granules (10 wt. %) are found to be 40 wt. % (Ca-LS), 45 wt. % (Na-LS) and 65 wt. % (KL) respectively.

The water content differences are the measure of the amount of water evaporated in the process. The energy requirement calculated for the evaporation and production of granules from one kilogram of liquid black liquor was 0.98 MJ for Ca-LS, 1.10 MJ for Na-LS and 1.59 MJ of KL. The energy requirement per kilogram of granules calculated based on their material flows (see chapter 6) are 3.84 MJ for Ca-LS, 4.31 MJ for Na-LS and 11.78 MJ for KL respectively. The total energy, including base energy, evaporation energy and pump energy would increase the values by 0.5 MJ per kilogram. The differences in the energy values of the granules measured and the energy required calculated based on the evaporation energy of water are 21.66 MJ kg^{-1} for CaLS, 20.19 MJ kg^{-1} for NaLS and 20.72 MJ kg^{-1} for KL respectively. The evaporation energy differences are represented with red coloured lines in figure 58b with red dotted (Na-LS, KL) and red dashed (Ca-LS) lines. The red dotted and dashed lines indicate that a positive energy balance can be only achieved with a minimum granule production amount of 500 g to 750 g per hour.

Even though the red (dashed and dotted) lines show a better positive balance, the spray granulator or spray drier requires extra process energy in the process apart from the evaporations energy indicating the blue reference lines to be more realistic. The positive energy balance can only be achieved when the throughput is more than one kilogram per hour.

Acid requirement of the respective acids (H_2SO_4 / CH_3COOH) are calculated empirically by observing the pH value change of the filtrate after filtration of granules. The pH value changes are shown in figure 59. The results show that there is no significant increase in the pH values, when the Ca-LS, Na-LS granules are treated with H_2SO_4 acid indicating highly efficient reaction with the granules.

The Kraft lignin (KL) granules treated with CH_3COOH show a high increase in the pH value with increasing mass of granules till a pH value of 3.7. After this the pH value increase is only nominal as this is where the buffer function of the acetate starts. The acetate buffer ranges in between pH values of 3.7 and 5.7 and is marked in figure 59 with blue colour. The amount of acid required is calculated from the pH value changes measured with respect to an increase in amount of granules.

In case of KL, the amount of acid required is calculated at a pH value of 5.7 and it is around 0.23 l to treat 330 g of granules (obtained from 1000 g of black liquor). Whereas in case of Ca-LS and Na-LS, there was no change in pH value indicating the acid can handle a higher amount of granules as long as enough acid in the liquid form is present to react with the granules. The acid requirement is approximated to range from 0.5 l to 0.7 l handling approximately 500 g to 550 g of granules.

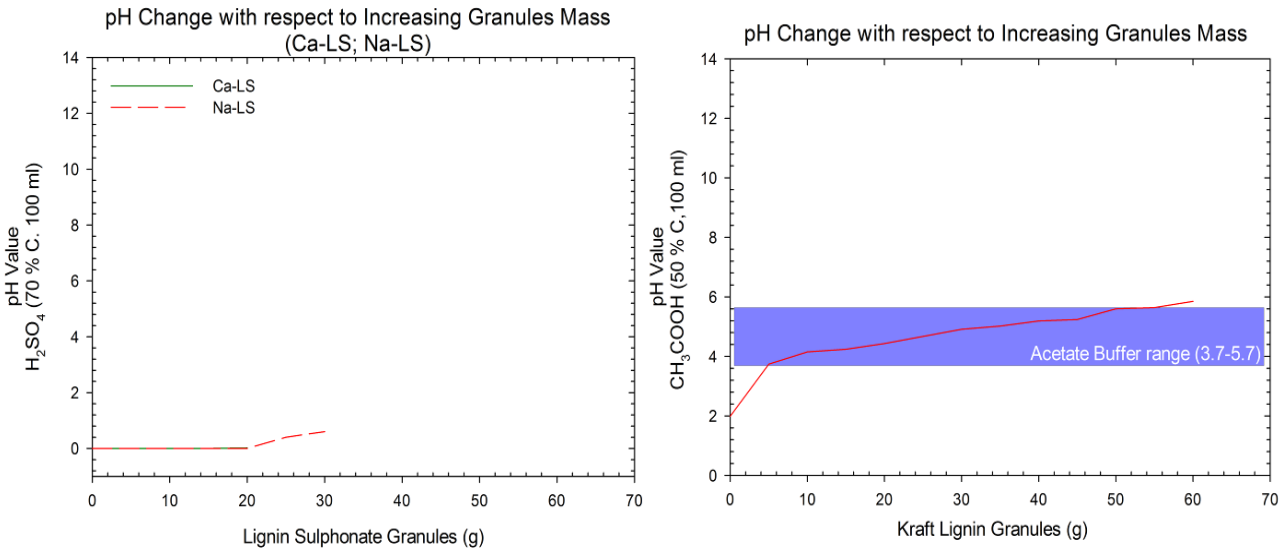


Figure 59: Empirical acid requirements measured by increasing the amount of granules and measuring the pH value changes.

The **acid and water regeneration** can be carried out using different methods such as contact towers, distillation, condensation, evaporation, liquefaction, crystallization, etc. The lignin sulphonate granules in the innovative process are treated with 70 % concentrated sulphuric acid under the influence of temperatures above 130 °C (optimal), leading to a strong gas formation consisting mainly of SO_2, CO_2, water vapor and H_2S. The Kraft lignin granules are treated with acetic acid resulting in conversion of inorganic compounds predominantly into sodium-acetate. The inorganically bound CO_2 and sulphur (S) in Kraft lignin are released as gases in the form of H_2S and CO_2.

The H_2S gas can be condensed and liquefied transforming it back into sulphuric acid (Ohman et al., 2010). Further the H_2S gas can be treated with the help of sodium hydroxide (NaOH), transforming it into sodium sulphide (Na_2S). This Na_2S can be used as pulping chemical in the pulping process making the chemical recovery process for the pulp industries. The SO_2 gases can also be liquefied using contact towers with the help of contact method by oxidizing it into sulfuric acid (Wiesenberger and Kircher, 2001).

The transformed sulphuric acid can also be made to react with NaOH to form sodium-sulphate, which is used as make-up chemical in the chemical recovery process of the pulping industry (Wiesenberger and Kircher, 2001; Winnacker, 2005). The sulphuric acid is mainly regenerated by liquefying the exhaust gases.

The regeneration of acetic acid (CH_3COOH) from filtrate 1 can be carried out by treating it with strong acids such as H_2SO_4 or HCL. The filtrate 1 is mainly concentrated sodium-acetate salt ($NaCH_3COO$). The acetic acid can be regained from this salt with the help of strong acids splitting it into sodium salts (ex. Na_2SO_4, NaCl) and acetic acid. The purified acetic acid and separation of sodium salts can be carried out using rectification columns, liquid-liquid extraction or distillation processes.

4.3 Utilization possibilities of lignin based on the structure of agglomerates

The acid treatment of lignin granules result in the development of numerous pores leading from the granule surface to the interior due to the exothermal reaction of inbound liquid with acids emitting gases. This phenomenon is observed in granules from inner core to the outer surface. The acid treatment of granules develops into a micro-porous sponge-like appearance, which is observed under the microscope (figure 60).

This structure of the granules allows for the preparation of structured compounds, broadening the application domain of technical lignins. After acid treatment, the granules show no dissolution but higher mechanical stability, low swelling and shrinkage with increased cross linked network structure. These properties enable the possibility of acid treated lignins utilization as encapsulation materials, filtration medium, etc.

The obtained lignin granules comprised of micro-pores after acid treatment as shown in figure 60. The micro-porous structure of the granules can be used for absorption and releasable containment of any of a wide variety of useful compositions similar to that of starch treated with enzyme amylase (see chapter 2). The absorption capacity of the granules is investigated with water and it is found that the granules can withhold water up to 5 times higher than their own weight. This absorption capacity indicates a possibility of the granules utilization as a storage medium for different liquids holding active ingredients.

The absorbed compositions can then be released from the granules to the surroundings through controlled release over a long time period. The controlled release is investigated by air drying the granules and measuring the water contents. The controlled release of liquids from the granules to the atmosphere was investigated at 30 °C in an oven (figure 61). The investigations were carried out with the granules after saturating them with water. Ca-LS granules resulted in lower liquid holding capacity compared to that of Na-LS granules. Figure 61 shows the controlled release of the retained liquid water to the surrounding atmosphere. Ca-LS and Na-LS granules could hold the liquids up to 55 hours and 100 hours respectively.

These characteristics of the granules enable them in their utilization as long-term fertilizers encapsulating the active ingredients and releasing them in a controlled way. Their use as fertilizers is advisable as lignin is a biodegradable natural polymer.

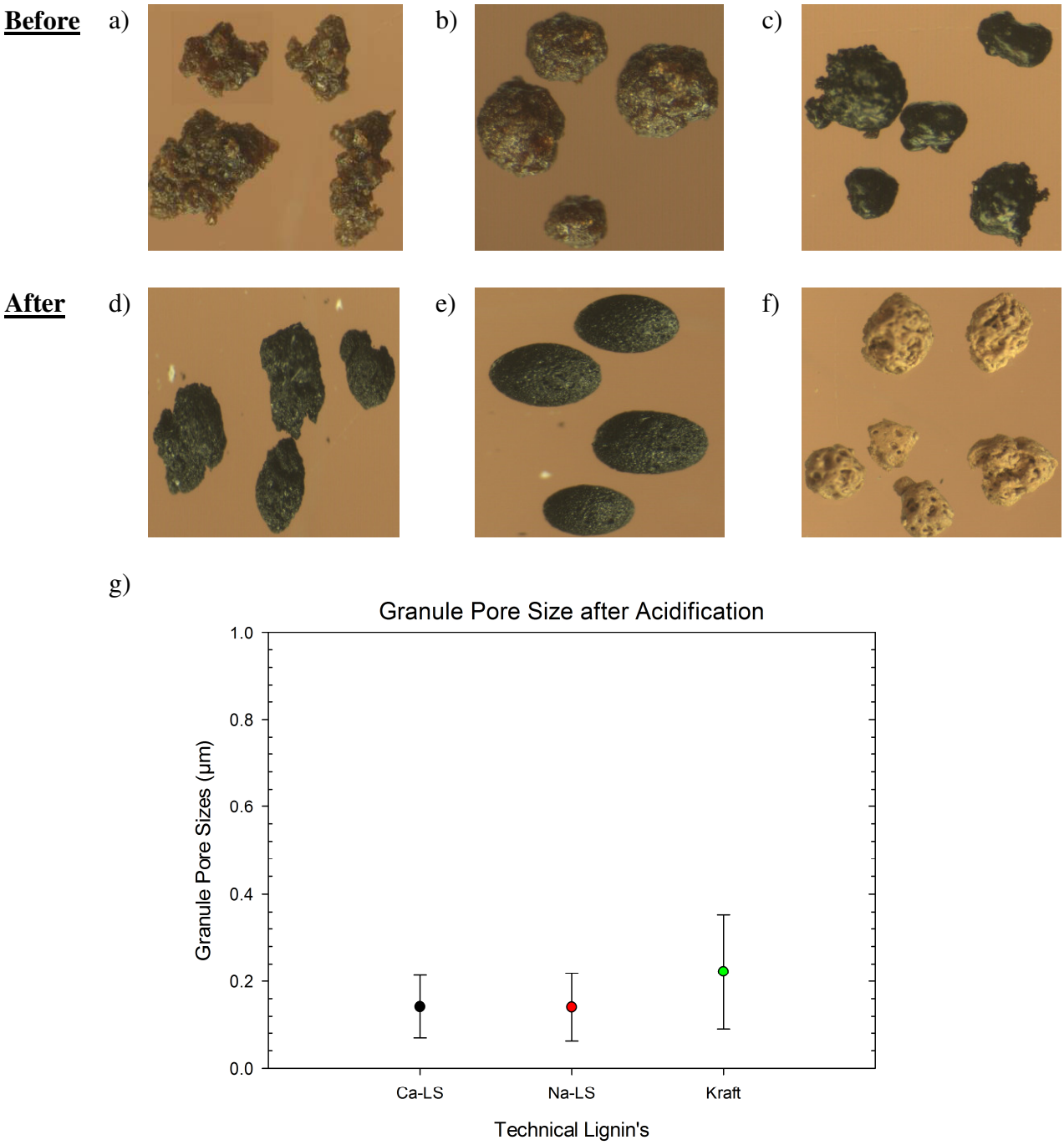


Figure 60: Granule structure before (a: Ca-LS; b: Na-LS; c: KL) and after (d: Ca-LS; e: Na-LS; f: KL) acidification along with the measured pore sizes (g) in granules.

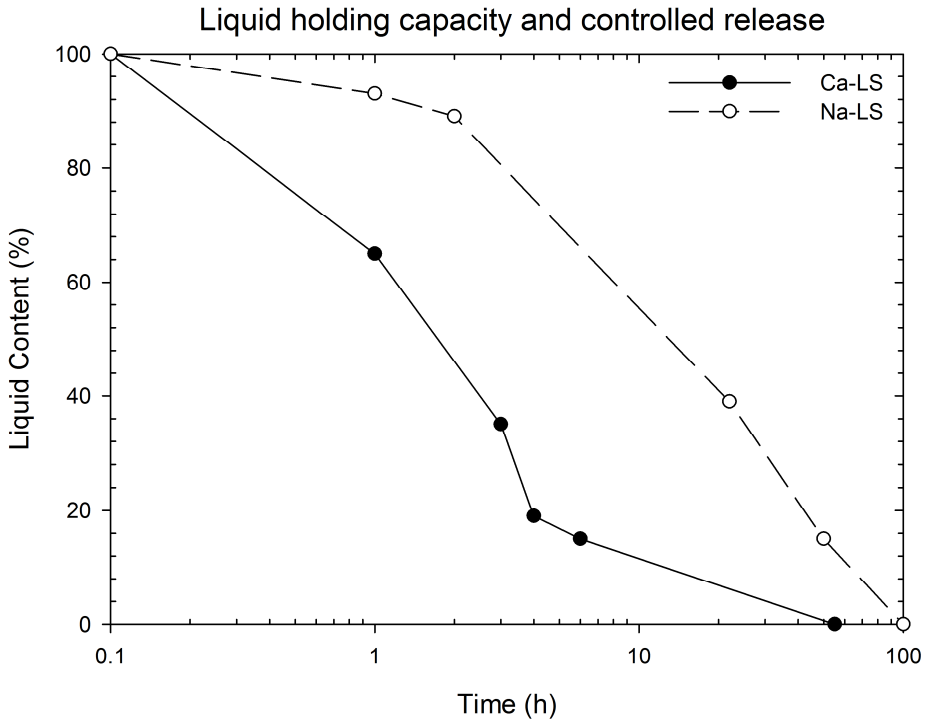


Figure 61: Liquid holding capacity and controlled release of liquids from produced lignin granules.

This work further modifies the existing patented process (Narra et al., 2012; patent application number 102010102327.1) producing hydrophobic micro-porous granules and produces acid stable micro-porous membranes (Narra et al., 2012; patent application number 102012109802.6) as shown in figure 62. The modification of the patented process is carried out by replacing the spray-granulator with dryer and heating plates. The dryer is used to dry the black liquors, obtaining dry lignin sludge powder.

The heating plates are used to press and melt the obtained dry lignin powder in a predefined form (circular, rectangular, etc.) as per the required membrane shape. The produced melt-press lignin is then treated with acids (H_2SO_4), which results in an acid stable micro-porous membrane. The produced membranes are stable and flexible in nature as long as they are in liquid medium or containing / retaining liquid inside them.

The drying of these membranes results in fissures / cracking of the membranes and are brittle in nature indicating that the produced membranes have to be stored in liquids. The strength / stability characteristics of the membrane can be improved by introducing a fiber network as a reinforcement of the structure making them also applicable in high pressure filtration processes.

Acid stable refers to the characteristics of the membrane in acids and states that the membrane remains intact and sustains useful membrane properties after its exposure to the acids. The production of acid stable membranes is only possible with lignin sulphonates (calcium lignin sulphonate in figure 62b and sodium lignin sulphonate in figure 62c). Kraft lignin does not result in stable membranes with the modified process, which can be due to the low molecular weight of the lignin from sulphate pulping reducing the binding effect. Secondly the production of Kraft lignin membranes in the pre-defined form with heat and pressure is possible, but the membranes are not stable due to the hygroscopic properties of Kraft lignin. Further the membrane does not retain its structure in the acid treatment process.

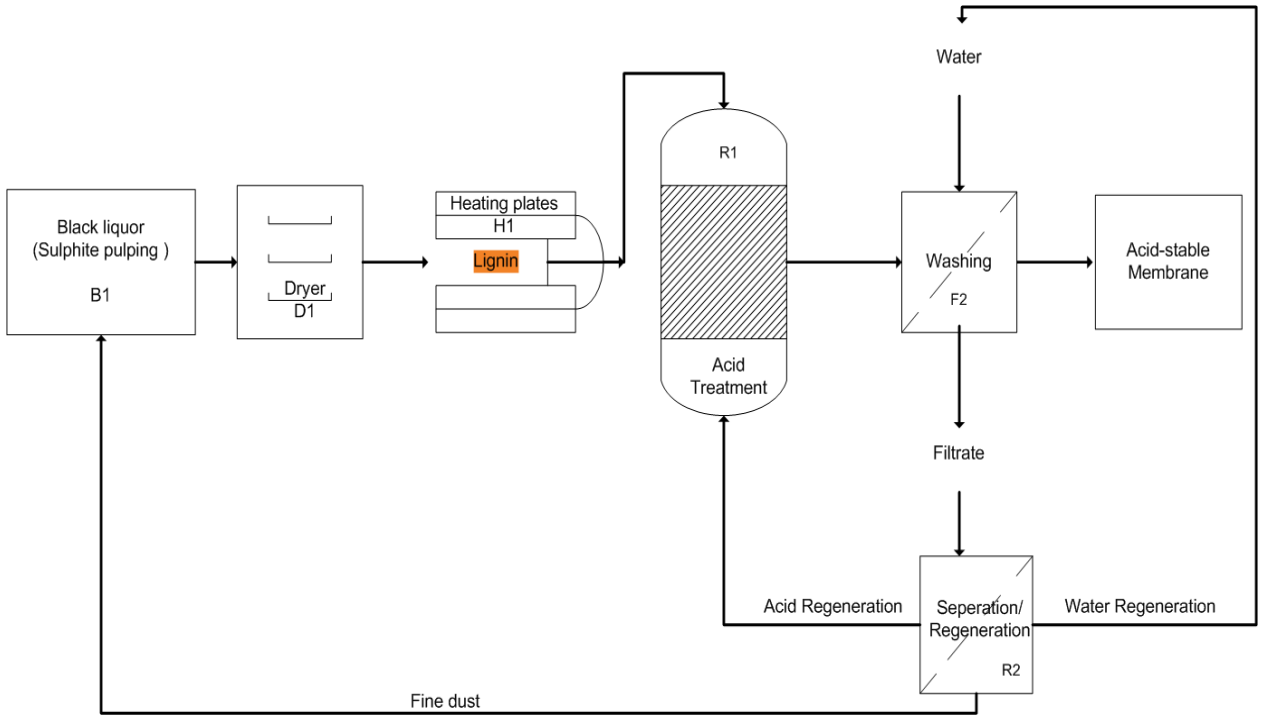
The membranes produced from calcium lignin sulphonate and sodium lignin sulphonate have pore sizes ranging in between 0.09 to 0.5 µm and 0.1 to 0.4 µm respectively. The measured pore sizes of the membranes are similar to that of the measured pore sizes from granules. Microfiltration membranes generally have micro-pores with a diameter greater than about 0.1 microns. The upper pore size limitation of microfiltration membranes is not well defined, but is limited to not be larger than 10 microns.

The microfiltration membranes are commonly used in filtration processes retaining small particles (fine dust, colloids, etc.) and microbes. The existing polymeric filtration membranes having acid stability are well known and are generally produced from polyolefins such as polyethylene, polypropylene, polyvinylidene flouride, polysulfones, polyethersulfone and polyether ketones (Kurth et al., 2006). The polymeric acid stable filtration mediums are essentially produced from fossil materials. The acid stable lignin filtration membrane is produced from a biogenic residue material, which can be used to substitute / replace fossil materials.

This work produces an acid stable microfiltration membrane from the biopolymer lignin obtained from paper and pulp industry residues and is especially applicable for the separation of components in a fluid mixture having low pH values and corrosive nature.

The produced micro-porous membrane can be used directly in the patented process of production of hydrophobic granules / briquettes and also in the modified process as a filtration medium separating the colloids / fine dust particles from the filtrate with the help of a filtration process. This separation of fine dust sized particles would simplify the acid and water regeneration process as after their separation the remaining liquid mainly contains of only acid-water mixture.

a)



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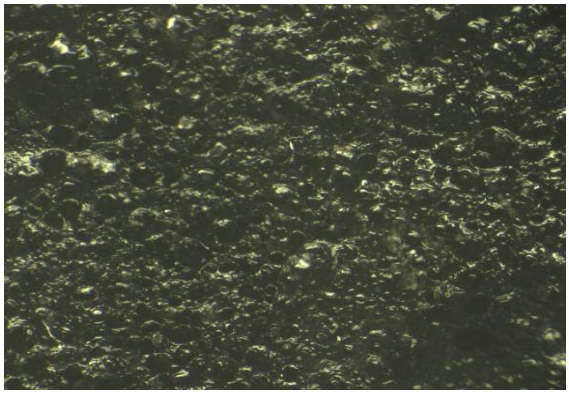

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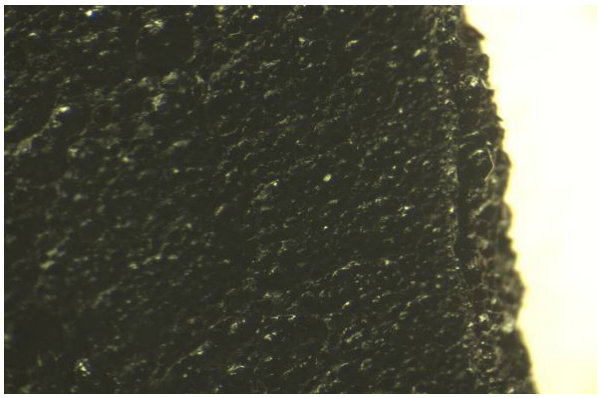


Figure 62: Micro-porous membrane production process (a) and the obtained calcium (b) and sodium (c) lignin sulphonate membranes observed under microscope.

Due to their liquids holding capacity the produced membranes can be applied in various industrial processes. Kurth et al., (2006) states that such kind of membranes can be used as semi-permeable membranes allowing efficient processing of many liquid based feed solutions. Kurth et al., (2006) also states that such kind of membranes can handle high amounts of feed at high permeating rates while maintaining the retention of dissolved metals, cat-ions, and organic compounds even in the presence of hot concentrated acids.

5. Biotechnological residues (publications 7 to 8)

This chapter deals with the production of fertilizer agglomerates from biotechnological (fermentation) residues. The production of these agglomerates is carried out conventionally using press-agglomeration processes after solid-liquid separation and after different pre-processing stages of both the phases, which are explained with process examples. Further this chapter also describes the innovative agglomeration processing possibilities with the help of encapsulation technology holding both solid and liquid phases together with or without pre-processing stages.

5.1 Processing of biogas residues

Maize biogas residues after the percolation step are utilized for agglomeration / encapsulation in this part of the thesis work. The water content of the residues is determined using ASAE Standard S 358.2 (ASAE 2006a), where oven drying of the samples is carried out at 105 °C for 24 h. In this process five samples are taken and the average moisture content is determined.

An impact mill (see also chapter 3) is used to **ground / comminute** the residues consecutively with the help of two different impact mill's screen sizes (10 mm and 6 mm). The impact mill is used to reduce the particle size of the residues into 10 mm and 6 mm consecutively in a step by step size reduction process. Reduction of particle size helps in improving the pelletisation process. The material is beaten until it is small enough to pass through the 10 mm sieve aperture size first and thus the obtained material is further comminuted with 6 mm sieve aperture size respectively. For the investigations, 50 kg of wet sample is comminuted into 10 mm and 6 mm particle sizes. The comminuted samples are shown in figure 63.

a)  b)  c) 

Figure 63: a) Biogas residues before grinding, biogas residues after grinding with 10 mm (b) and 6 mm (c) sieve aperture size.

Particle size analysis (image analysis) is carried out with the help of Fibreshape from Innovative Sintering Technologies using a flatbed film scanner at a resolution of 1200 dpi (see chapter 3). Fibreshape is specially chosen due to the reason that biogas residues are wet and sticky (figure 64a), which makes it difficult to measure the particle size analysis of single particles. This can only be carried out when the particles are dispersed in liquids. The flatbed film scanner of Fibreshape offers a large flat surface area, on which a Petri-dish is placed filled with water and the fibres are made to disperse in the liquid (water) as shown in figure 64 (b - g).

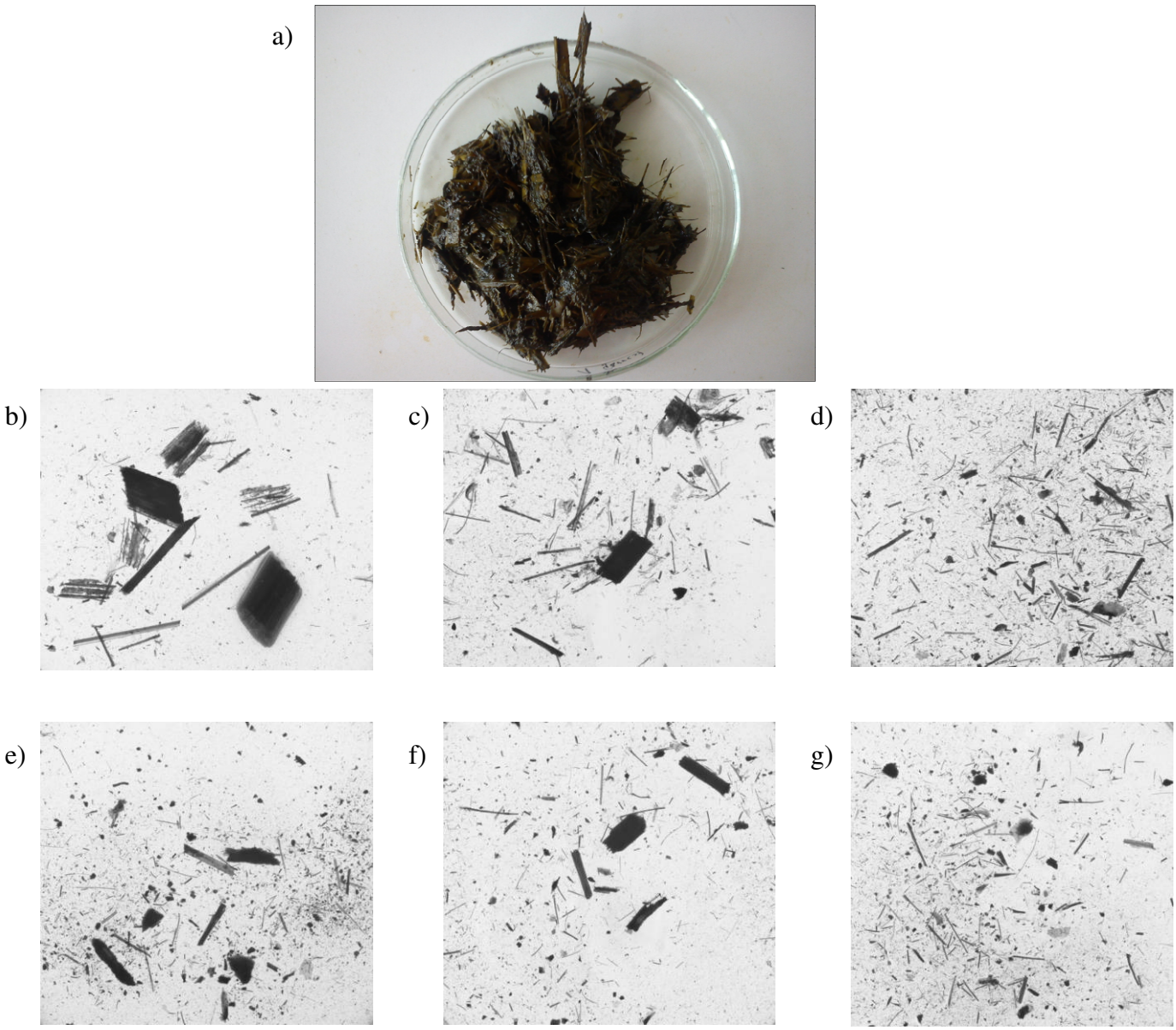


Figure 64: Biogas residues (a) suspended and dispersed in liquid inside petri-dishes (b – g) and are then scanned (grey-scales) using a flatbed film scanner for particle size image analysis using Fibreshape.

The **agglomerates** from the biogas residues are produced using three different methods, (i) build-up agglomeration of biogas residues with additive and binder mixtures (lime, starch, gelatin and carboxymethylcellulose - CMC) in an Eirich-intensive mixer (working on the principle of pelleting discs) after comminution with an impact mill having 10 mm and 6 mm classifier sieves, (ii) press agglomeration of residues after dewatering with centrifugal forces is carried out in a KAHL press pelleting machine, and (iii) encapsulation of residues with / without pre-processing stages.

Build-up agglomeration of biogas residues is carried out with the help of a rotating build-up disc (figure 65a) and an Eirich-intensive mixer (type R01), both of them working on the process principle of pelleting discs (figure 65). The Eirich-intensive mixer (figure 65b) consists mainly of three different components: (1) mixing pan, (2) mixing tool and (3) stationary scraper tool. The volume of the mixing pan used is 10 liters. The basic principal of the mixer is that the rotating mixing pan allows the material mixture into the area of the mixing tools. The mixing tool is arranged eccentrically and rotates in counter direction to the pan. The counter rotations of the mixing pan and the mixing tool create counter currents in the material and thus influence the agglomeration / pelletisation process.

a) b)

c) d) e) f)

Figure 65: a) Rotating build-up pelleting disk b) Eirich-intensive mixer (type R01). The utilities of Eirich mixer are listed below as c) mixing pan of size 10 liter d) mixing tool with pointed ends (left), formation of pellets is not observed e) mixing tool (right) with scattered wings successful in pellets formation and f) stationary scraper tool.

Press agglomeration / pelletisation is the densification process of solid materials with pressure. Press pelletisation requires removal of water (dewatering). Pellets are prepared with the solid residues after dewatering using the KAHL press pelleting machine (figure 66). The working principle is similar to that of the flat mould / die press pelletisation process. The material is fed towards the flat mould having 6 mm diameter and 40 mm length apertures. The temperature measured during the pelletisation process is between 40 °C to 70 °C.

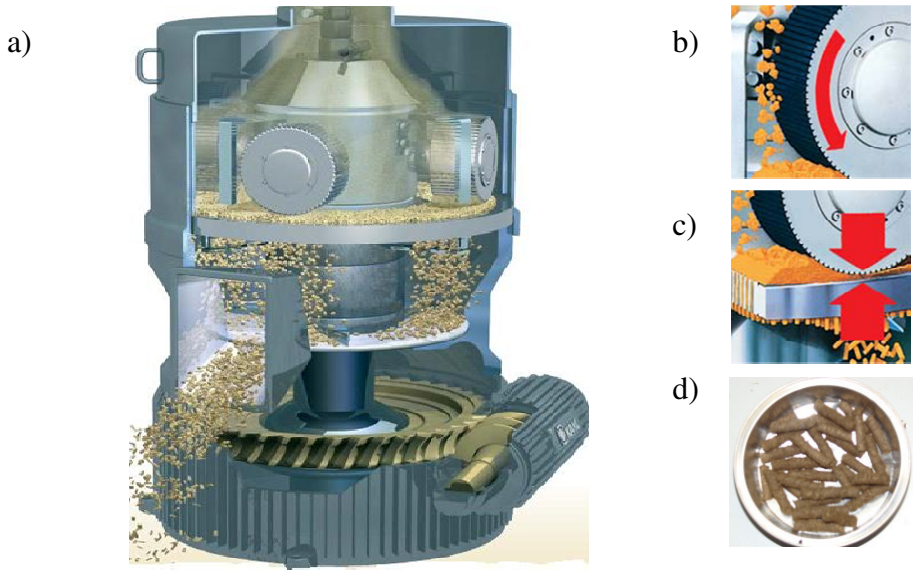


Figure 66: a) Structure of KAHL Pelleting Press used for compaction, b) good aeration of material due to free falling particles, c) pelleting through high pressure rollers and d) produced pellets.

The solid-liquid separation (dewatering) is achieved with the help of a centrifuge (Krauss Maffei process technology type: test-centrifuge HZ 25 as shown in figure 67). The dewatering of the biogas residues is carried out before and after comminution with impact mills having 6 mm and 10 mm sieve aperture sizes. The centrifugal efficiency of the biogas residues with the used centrifuge is measured by determining the amount (weight) of water / liquid separated with respect to time.

a)

b)

c)

Figure 67: a) Krauss Maffei process technology (type: test-centrifuge HZ 25) used in dewatering of biogas residues, b) solid material after dewatering inside the centrifuge, c) solid material from the centrifuge after air drying.

Encapsulation (capsule / cachet filling) of fermentation residues, and the usage of encapsulated residue agglomerates (capsules) provide an optimal solution for the long term controlled release of nutrients into the soil increasing the soil fertility due to holding of both solid and liquid phases together simultaneously improving the plant yield and reducing the intensified fertilizer utilization. This process also includes various production possibilities such as single, multiple, porous and enclosed encapsulations in various shapes and sizes such as spherical, cylindrical, conical, rectangular, etc. This work tries to use biodegradable / renewable polymers (PLA, starch and alginate in combination, alginate, polyethylene and lignin) as encapsulation materials enabling the produced capsules utilization as fertilizers without any further concerns regarding fertilization standards, soil standards, environmental standards, etc. The biopolymers are used in the direct as well as in indirect enclosed encapsulation of fermentation residues.

This thesis work mainly uses build-up agglomeration processing with the help of pelleting discs or mixers and presents various encapsulation possibilities (with or without dewatering, with or without grinding, with or without binders, with or without additives, single or multiple encapsulations, porous or enclosed encapsulations, etc. and their combinations) as shown in figure 68 and displays the various intermediate and end products as process examples. The build-up agglomeration process also allows the addition of additives / binders to improve the suitable fertilization effect for each specific soil type.

The process paths “direct or indirect encapsulation” and the pre-processing stages (dewatering, grinding, etc.) can be chosen based on the fermentation residue characteristics (solid-liquid, liquid-liquid mixtures) and can be optimized with additives or binders based upon the soil requirements and automated fertilizing machines. The process paths shown in figure 68 are chosen in such way that the innovative encapsulation process can be easily integrated into the presently existing fermentation plants using conventional processes. Further the process examples and their intermediate and end products are listed separately with the pre-processing choices and display either intermediate products or end-products.

Intermediate **products one** and **three** are produced with the help of build-up agglomeration process using pelleting disks or pelleting mixers. Depending on the fermentation residue characteristics and on the desired end product, several preprocessing stages (with or without dewatering, with or without grinding, with or without binders, with or without additives, etc.) can be applied. Intermediate products are porous agglomerates.

End **products two** and **five** are achieved by direct encapsulation using biopolymers as encapsulation materials. End product two is encapsulated with the solid-liquid mixture fermentation residues without applying preprocessing stages. The pre-processing stages are optional and can be selected depending on the characteristics of the fermentation residues. End product five can be achieved by encapsulating the liquids either directly from the liquid-liquid mixture fermentation residues or from the solid-liquid mixture fermentation residues after dewatering. End products two and five are single encapsulated enclosed capsules.

End **product four** encapsulates the intermediate products as well as the liquid capsules inside the fibres as a core or in the matrix form. The intermediate products (product one, product three) can be encapsulated with alginate-/ bio-polymers as encapsulating materials and transform either into product two or product four. End product five is further encapsulated inside the fibres either as core or in the matrix form to achieve end product four. Product four is achieved using various optional preprocessing stages depending on the fermentation residues characteristics and on the desired end product characteristics. End product four is multiple encapsulated enclosed capsules.

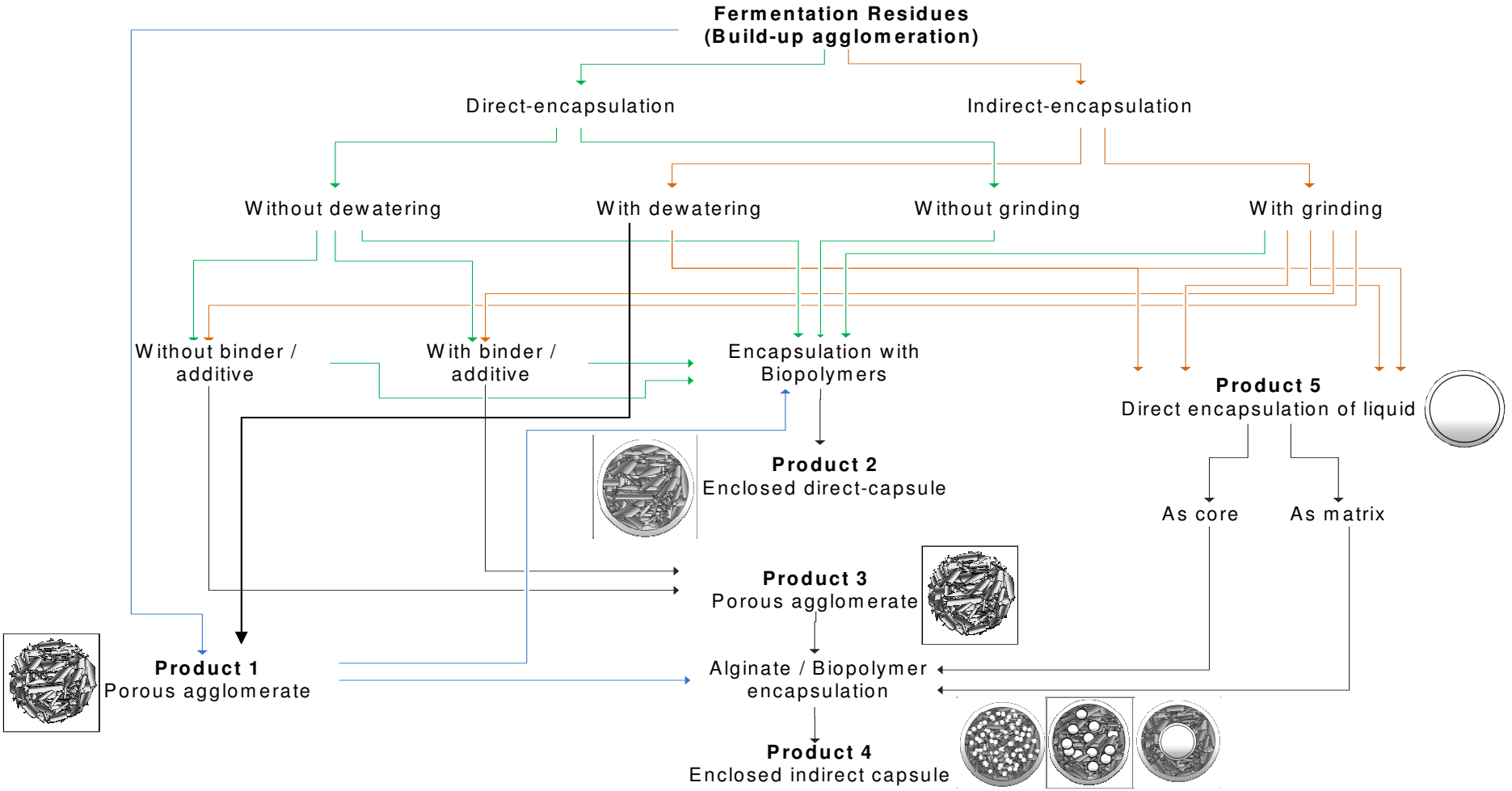


Figure 68: Encapsulation processing possibilities with various intermediate products (product 1, product 3 and product 5) and end products (product 2, product 4 and product 5).

Agglomeration / pelletisation is carried out using different pre-processing stages, different additives, and different pelleting processes. The materials for build-up pellets are prepared with increasing amounts of additives and binders. Lime (40 wt. % to 50 wt. %) is chosen as additive, whereas starch (7.5 wt. % to 20 wt. %), gelatin (10 wt. % to 30 wt. %) and CMC (2.5 wt. % to 10 wt. %) are chosen as binders. The binders are chosen in such a way that they can bind both the solids and liquids together and the additives are chosen in such a way that they improve the fertilization effect. In the second step press pelletisation of the residues is carried out after dewatering the residues with centrifugal forces; the dewatering process increases the dry substance concentration of the materials from 15 wt. % to 80 wt. %. The press pelletisation process further densifies the solid fiber materials after dewatering into cylindrical pellets.

The encapsulation is carried out with alginate, lignin granules (chapter 4), gelatin capsules and PLA. Alginate is used after the build-up agglomeration process of the residues with binders (starch, gelatin, CMC, etc.) in the indirect encapsulation process (product 4). The liquids after the solid liquid separation are also encapsulated with alginate in the direct encapsulation process (product 5), which can be used either as intermediate product or end product. The liquids are also encapsulated in the lignin granules (Ca-LS and Na-LS) utilizing their liquid holding capacities. The liquid holding capacities can be increased by encapsulating them with alginate. The encapsulation with gelatin capsules is carried out including the preprocessing stage dewatering and a combination of alginate encapsulated liquids along with solid fibres producing multiple encapsulated enclosed capsules (product 4) is investigated. PLA is used in the direct enclosed encapsulation of the biogas residues without any preprocessing stages.

The various agglomeration mixtures of the substrates used for build-up agglomeration, press agglomeration and encapsulation are given in table 13. The different mixtures and their variants are denoted respectively for lime as L1 to L12 with decreasing concentrations of lime from 50 wt. % to 40 wt. % for the 6 mm (L1 to L6) and 10 mm (L7 to L12) comminuted residues, for starch with decreasing concentration from 20 wt. % to 7.5 wt. % as S1 to S3, gelatin with decreasing concentration from 30 wt. % to 10 wt. % as G1 to G3, for carboxymethylcellulose (CMC) with decreasing concentrations from 10 wt. % to 2.5 wt. % as CMC1 to CMC3, for encapsulation of liquid from liquid-liquid mixtures or solid-liquid mixture after dewatering with alginate as AL1, encapsulation of liquids with lignin granules as LG1 for Ca-LS and LG2 for Na-LS granules, different capsules prepared with alginate after build-up agglomeration with different binders such as starch, gelatin and CMC are denoted as AL-S1 to AL-S3, AL-G1 to AL-G3, and AL-CMC1 to AL-CMC3 respectively. The alginate encapsulation of lignin granules are denoted as AL-LG1 and AL-LG2. Further gelatin capsules and polylacticacid (PLA) biopolymer foils are used in the direct encapsulation of biogas residue materials and are denoted as GC1 to GC3 and PLA respectively. Press agglomerates produced after comminution with impact mills (having 6 mm and 10 mm sieve aperture sizes) and dewatering with the centrifuge are denoted as C1 and C2.

Table 13: Biogas residue mixture compositions with additives, binders and their respective variants in weight % from build-up agglomeration, press agglomeration and encapsulation processes. (L*: Liquid in percentage).

	Variants	Wet Residues (wt. %)				Additives / Binders (wt. %)				Products
		6 mm	10 mm	Dewatering 6mm	Dewatering 10mm	Lime (%)	Starch (%)	Gelatin (%)	CMC (%)	
Additive	L1	50				50				Product 3
	L2	52				48				
	L3	54				46				
	L4	56				44				
	L5	58				42				
	L6	60				40				
	L7		50			50				
	L8		52			48				
	L9		54			46				
	L10		56			44				
	L11		58			42				
	L12		60			40				
Binders	S1			92.5			7.5			Product 3
	S2			90			10			
	S3			80			20			
	G1				90			10		
	G2				80			20		
	G3				70			30		
	CMC1		97.5						2.5	
	CMC2		92.5						7.5	
	CMC3		90						10	
Encapsulation	AL1				L*:100					Product 5
	LG1				L*:100					
	LG2				L*:100					
	AL-S1			92.5			7.5			Product 4
	AL-S2			90			10			
	AL-S3			80			20			
	AL-G1				92.5			7.5		
	AL-G2				90			10		
	AL-G3				80			20		
	AL-CMC1		97.5						2.5	
	AL-CMC2		92.5						7.5	
	AL-CMC3		90						10	
	AL-LG1				L*:100					
	AL-LG2				L*:100					
	GC1		100							Product 2
	GC2				100					
	GC3		50% GC2 + 50% AL1							
	PLA		100							
Cent	C1				100					Product 1
	C2			100						

The produced agglomerates are then tested for abrasion and strength. **Abrasion** is a very important mechanical property for the storage and transportation of pellets. Abrasion is measured using two rotating crates depending upon the types of the agglomerates. Abrasion of the build-up pellets is carried out with a smaller quadratic crate (L × B × D: 10 × 10 × 5 cm^3) and for the press-agglomerates after dewatering with a bigger quadratic crate (L × B × D: 30 × 30 × 12 cm^3) as shown in figure 69b and figure 69a respectively. The quadratic crate rotates at a speed of 50 rpm for 10 min. The sample is then sieved with a sieve having an aperture size of 500 µm for build-up agglomerates and 1.25 mm for press agglomerates. The different sieves (0.8*diameter) are specifically chosen based on the diameter of the produced agglomerates as suggested by Thomas and Van der Poel, (1996). The difference in the weights of the agglomerates before and after the abrasion test gives the abrasion value (see also chapter 3).

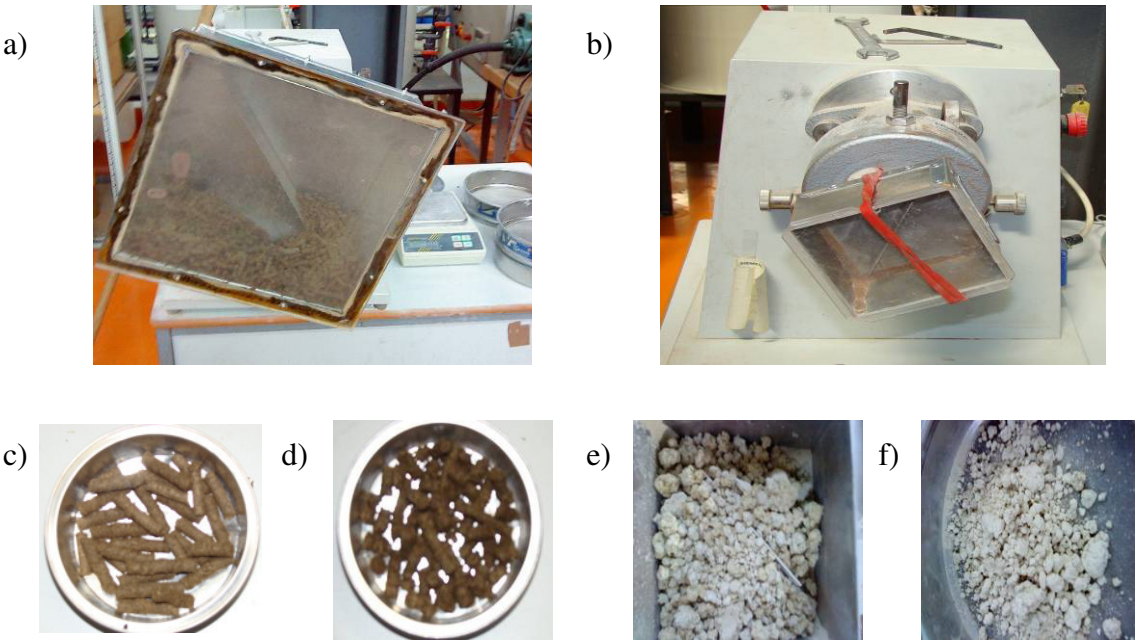


Figure 69: a) Bigger- and b) smaller rotating quadratic crate for measuring the abrasion of pellets. c) and d) are the press pellets before and after abrasion, whereas e) and f) are the build-up pellets before and after abrasion respectively.

The **strength** of the pellets is evaluated using a material testing (tensile and compressive strengths) machine (ZWICK-ROELL type: ZMART.PRO). The diametrical strength tests (figure 70) are carried out for all kinds of agglomerates produced. The diametrical strength tests are carried out as these forces occur during handling, transportation and storage of the agglomerates. This test is specifically chosen due to its applicability on all kinds of produced agglomerates using different agglomeration processes (build-up, press, encapsulated capsules).

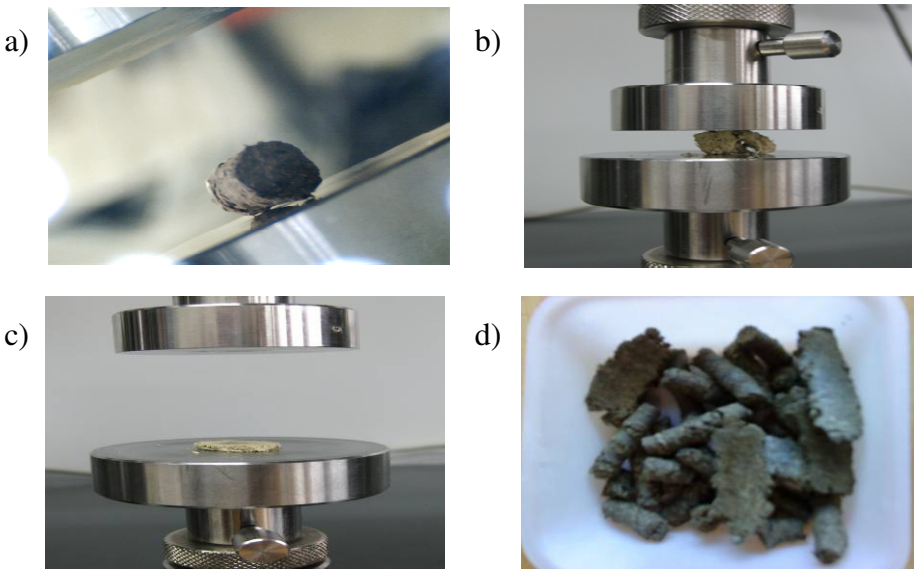


Figure 70: a) Press pellet for diametrical strength-test, b) build-up pellet during strength test, c) and d) show the build-up and press pellets after different strength tests.

The **nitrogen content** of the biogas residues and the produced agglomerates are determined using the Kjedahl nitrogen test method (figure 71). The Kjedahl nitrogen test method mainly involves three different steps, which are i) digestion, ii) distillation and iii) titration. Digestion is accomplished by dissolving the samples in concentrated sulphuric acid (H_2SO_4), resulting in an ammonium sulphate ($(NH_4)_2SO_4$) solution as given in equation 9. Sodium hydroxide (NaOH) is added as excess base to the digested product in the distillation converting NH_4 to NH_3 and the NH_3 is subsequently recovered as product (equation 10). The third step titration quantifies the amount of ammonia in the receiving solution with a change in colour as indication of the completed titration. The amount of nitrogen is calculated from the quantified amount of ammonia. The titration can be either back titration or direct titration. This work uses direct titration with boric acid as receiving solution and the chemical reactions taking place are as given in equation 11 and equation 12.

$$\text{Organic N} + H_2SO_4 \rightarrow (NH_4)_2SO_4 + H_2 + CO_4 + \text{Byproducts} \quad (9)$$

$$(NH_4)_2SO_4 + 2NaOH \rightarrow 2NH_3 + Na_2SO_4 + 2H_2O \quad (10)$$

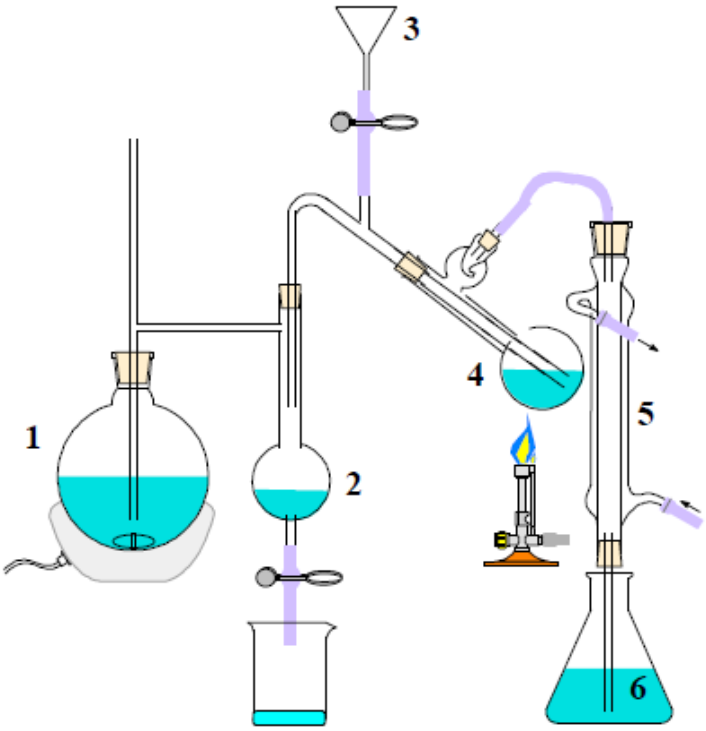
$$NH_3 + H_3BO_3 \rightarrow NH_4 + H_2BO_3^- + H_3BO_3(\text{excess}) \quad (11)$$

(colour change occurs)

$$2NH_4 + H_2BO_3^- + H_2SO_4(NH_4)_2SO_4 + 2H_3BO_3 \quad (12)$$

(colour change occurs in reverse)

The direct titration method is chosen as this method only requires one standard solution having long shelf life. The boric acid captures ammonia gas developing into an ammonium-borate complex and the change in colour (from green to violet as shown in figure 71) is observed with increasing concentrations of ammonia collection.



1 Steam producer

2 Water separator

3 NaOH supply

4 Kjeldahl flask with acid digestion

5 Cooler drip-catcher

6 Defined acid concentration + indicator

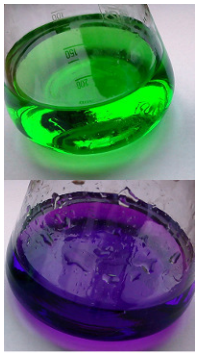


Figure 71: Ammonium distillation with water vapor according to acid digestion method (a) and the colour change of the solution from green to violet after titration (b).

5.2 Results and discussions based on the processing of biogas residues

The **water content** of the biogas residues measured is ranging between 80 wt. % to 85 wt. %. The **particle size distributions** of the fermentation residues analyzed before and after the comminution process with an impact mill having 6 mm and 10 mm classifier sieve aperture size are depicted in figure 72. The distribution curves start from 21 µm as the resolution of the scanner is set to 1200 dpi. The particles are classified into different particle size classes, which are long particles (length: 800 µm and above, width: 80 µm and above), short particles (length: 200 – 800 µm, width: 25 – 80 µm), slime stuff (length: upto 200 µm, width: upto 1 µm) and flour (length: 20 - 200 µm, width: 1 – 30 µm) (see chapter 2). Long particles and short particles are fibrous materials, whereas the slime stuff and flour stuff are fines (Pruden, 2005). The results show that 100 % of the fermentation residue particles can be classified as long particles. The fermentation residues particles after comminution with impact mills having 10 mm (red) and 6 mm (green) classifier aperture size show an increase in short particles up to 10 % and the remaining 90 % of the particles remain long particles. A significant reduction of particle sizes is observed with the comminution (figure 72). The difference in particle sizes of the biogas residues after comminution with the impact mill having 10 mm and 6 mm classifier is also observed. However the particle size distribution after 6 mm comminution shows a uniform particle distribution between D20 and D80, whereas after 10 mm comminution the uniform particle size distribution is only observed between D20 and D40.

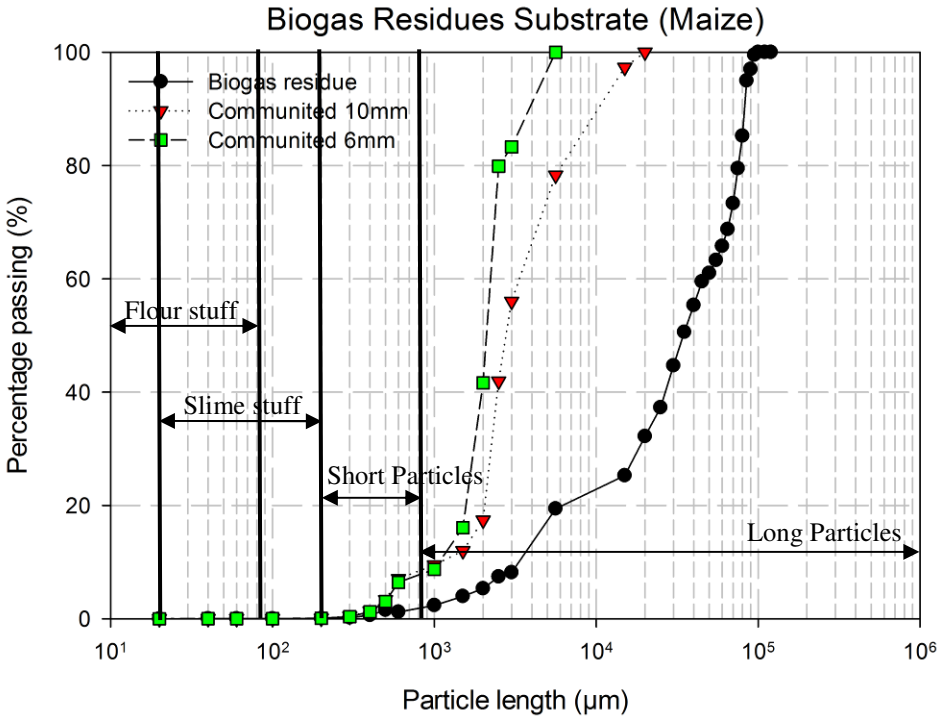


Figure 72: Particle size distribution of the biogas residues, comminuted with classifier sieve apertures of 10 mm and 6 mm.

The particle size distribution of the fermentation residues play a very important role in the build-up as well as in the press agglomeration and encapsulation processes. The automated processing of higher size particles is difficult due to the i) long particle size of fibres blocking the moulds especially in the press agglomeration process (see chapter 3), ii) elasticity of the fibres in bending is higher causing problems in building-up of agglomerates and iii) encapsulation is difficult due to non-homogenous filling of ingredients. The elasticity of the fibres reduces with increasing moisture content as the water molecules in the fibres act like a plasticizer indicating low elastic modulus and low tensile strength but high compressive strength of the fibres (Nair, 2010). The high compressive strength of fibres along with high moisture contents make the build-up and press agglomeration process more complicated and tedious.

The comminution of wet biogas residues in impact mills with 10 mm and 6 mm classifier sieve aperture sizes consecutively in a step by step process is highly tedious due to (i) difficulties in feeding of the material, (ii) sticking of the residue materials to the machinery, (iii) high moisture contents, etc. These are the main reasons that in the conventional process first the dewatering and then the comminution followed by the agglomeration process is carried out. The dewatering of the residues increases the comminution efficiency of the used machine and is more efficient.

The **dewatering efficiency** of biogas residues before and after comminution is measured with the help of a laboratory centrifuge with respect to time and is displayed in figure 73. The dewatering is carried out directly with the biogas residues before and after comminution in impact mills with 10 mm and 6 mm sieve aperture sizes to verify the dewatering efficiency with respect to the varying (reducing) particles sizes. 85 wt. % of average water contents are measured and is noted in the graph with the red line. The dewatering efficiency is calculated as ratio of the maximum separated water contents to the average water contents (85 wt. %) in percentage and are respectively represented in figure 73 with percentages and black arrow lines. The maximum dewatering achieved is around 70 wt. % to 75 wt. % (dewatering efficiency of approx. 85 %) water removal from the residues before comminution. The 10 mm comminuted particles resulted in 43 wt. % (dewatering efficiency of 51 %) water removal after a time period of 70 minutes. The 6 mm comminuted particles resulted only in a maximum of 30 wt. % water removal (dewatering efficiency of 35 %). The solid liquid separation of the biogas residues is also tedious and results only in a maximum dewatering efficiency of 85 %. The dewatering efficiency with its high efficiency from non-comminuted particles indicates that the process becomes easier, when the residues are first dewatered and secondly comminuted followed by agglomeration processes.

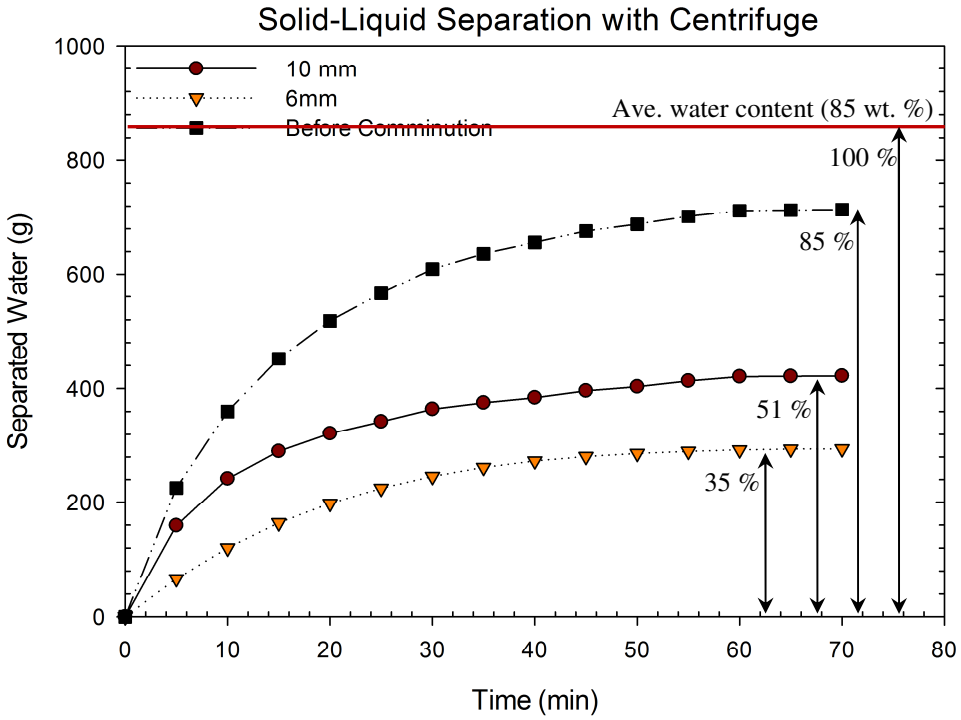


Figure 73: Dewatering efficiency of the biogas residues before and after comminution with respect to time.

An optimized speed for the **production of build-up agglomerates** in the Eirich-intensive mixer is determined at 3000 rpm and by employing the mixing tool having scattered wings. At this speed agglomerates of regular shape and size are achieved within the time period of one to three minutes depending on the different mixture ratios of additives, binders, etc. It is noticed that the mixture with higher concentrations of lime took longer time to form pellets as compared to that of the mixtures with lower concentrations of lime. Similarly it is easier to produce agglomerates with binders such as starch, gelatin and CMC at lower concentrations then compared to that at higher concentrations.

From 10 to 40 wt. % of the lime and 60 to 90 wt. % residue mixtures do not build-up into agglomerates, rather a cake type of mixture is obtained. Further 40 to 50 wt. % of lime with biogas residues mixture helps in the building-up of agglomerates. Similarly the build-up agglomeration with binders is only possible for (i) starch in between 7.5 wt. % and 20 wt. % mixtures, (ii) gelatin in between 10 wt. % and 30 wt. % mixtures and (iii) CMC in between 2.5 wt. % and 10 wt. % mixtures respectively. 46 wt. % lime mixture results in better agglomerate formation within a time period of one minute 50 seconds and the obtained agglomerates are having regular size and shape. The water content in the agglomerates are found to be 35 wt. % (directly measured after agglomeration formation) and the agglomerates after stabilization for 7 days have a water content of around 5 wt. %.

Press agglomeration of the solid materials after dewatering (solid-liquid separation) is successfully carried out with both 10 mm and 6 mm comminuted biogas residues. The water content of the press agglomerates measured directly after production are ranging in between 20 wt. % to 25 wt. % and after stabilization are in between 5 wt. % and 7 wt. % respectively. The separated liquids are then encapsulated with alginate as an intermediate product (multiple encapsulations) or end product (single encapsulation).

The **encapsulation** (indirect) with alginate (one layer and two layers) is possible with all the successfully produced build-up agglomerates as well as with the separated liquids. The direct encapsulations of biogas residues without any preprocessing steps are also successfully carried out with the help of gelatin capsules and PLA foils. The encapsulation of the liquids (variants AL1, LG1 and LG2) after solid-liquid separation is successfully carried out with alginate (alginate capsules). Further the multiple encapsulations are carried out by combining the liquid alginate capsules and the separated fibres and filling them inside the gelatin capsules. Figure 74 displays all the produced agglomerates from different process steps including the encapsulations.

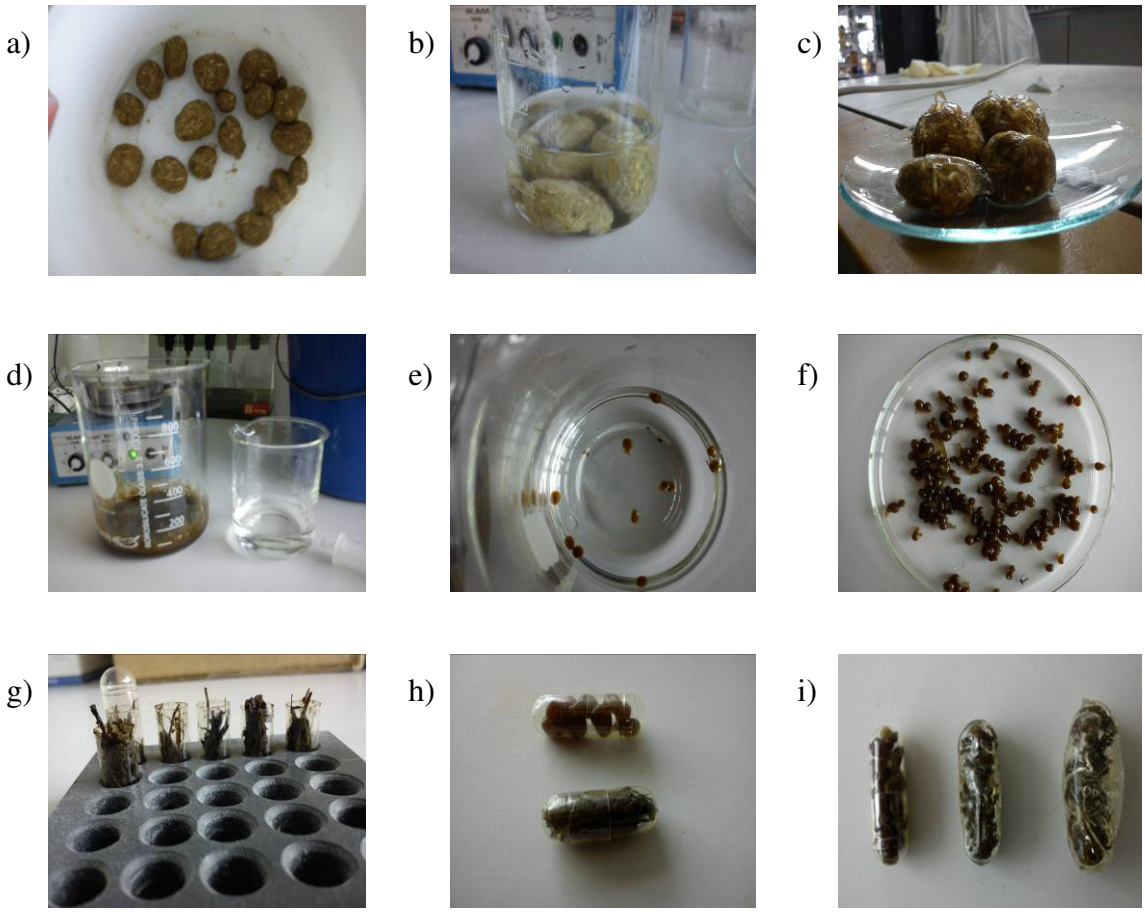


Figure 74: Production of build-up agglomerates (a) with different binders and encapsulation with alginate (b and c), encapsulation of separated liquids with alginate (d to f) and encapsulation of liquids and fibres in gelatin capsules (g to i).

Abrasion and strength are used as quality controlling characteristics of the produced agglomerates. The **abrasion** results of the build-up, press and encapsulated agglomerates are displayed in figure 75. The agglomerates produced with additives (lime) (product 3) displayed significant differences in the abrasion results with respect to the particle sizes. The 6 mm (L1 to L6) comminuted residues result in lower abrasion values in comparison to those of the 10 mm (L7 to L12) comminuted residues.

The press agglomerates produced with the solid materials after dewatering (product 1) also result in lower abrasion (1.4 %) with the 6 mm comminuted residues (C2) in comparison to those with the 10 mm (4.5 %) comminuted residues (C1). The abrasion results from both build-up as well as the press agglomeration processes indicate a significant relation to the particle sizes of the residue materials.

The build-up agglomerates L3 (46 wt. % lime) after comminution with 6 mm has the lowest abrasion value (6.7 %) among the additives group L1 to L6. The build-up agglomerates L9 (10 mm comminuted residues with 46 wt. % lime mix) give the lowest abrasion values (11 %) among the pellets group L7 to L12. The abrasion values of 10 mm comminuted residues with additive lime are higher than that of the 6 mm comminuted residues. The high abrasion of 10 mm comminuted residues is due to the high stiffness of the fibres in their wet state resulting in reduced interlocking and low binding effect.

The build-up agglomerates with binders (product 3) show comparatively lower abrasion values compared to that of the agglomerates with additive lime. Only the binder gelatin results in higher abrasion values, this can be due to the brittleness of the gelatin in dry state. The reaction of gelatin with the moisture content functioning as plasticizer and imparts flexibility leading into the bonding of various materials. When the bonded agglomerates are dried the gelatin regains its hardness and becomes brittle (Chang et al., 1998). This is the main reason that the build-up agglomerates produced with the binder gelatin after stabilization result in higher abrasion values. Similarly this also happens with the variant alginate encapsulated gelatin capsules.

Starch binder variants (S1 to S3) result in lower abrasion values compared to that of gelatin variants, but are higher when compared with CMC variants. The binder CMC results as the best binder having very low abrasion values. This can be due to the reason that CMC has high moisture binding capacities (up to 35 %) in comparison to the other binders (Hoefler, 2012). The abrasion values obtained from the CMC variants are almost comparable to that of centrifuged variants. The alginate encapsulated binder variants (product 4) result in reduced abrasion values in comparison to the agglomerates produced only with binders.

The direct encapsulation variants (product 2) with gelatin capsules (GC) and polylacticacid (PLA) also result in lower abrasion values, which can be due to the reason that fractionation of these capsules does not occur due to their rolling behavior in the abrasion testing machine. The direct encapsulation of liquids (AL1, LG1 and LG2) showed the lowest abrasion.

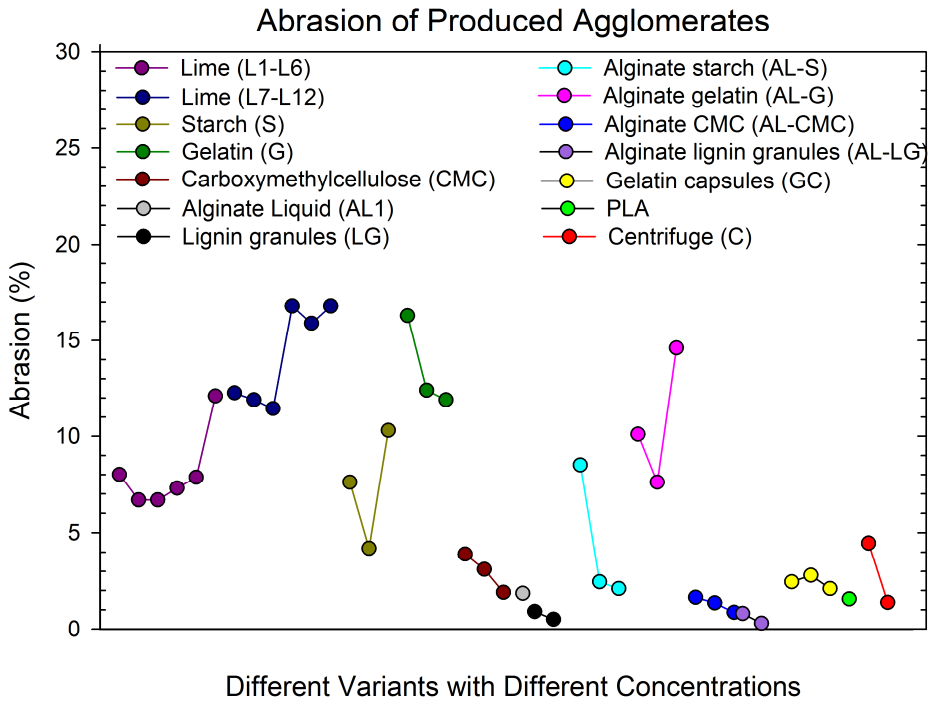


Figure 75: Abrasion value of the biogas residues variants.

The **strength** (diametrical force) of the different agglomerate variants is shown in figure 76. Agglomerates need to withstand different forces as they are confronted to such pressures during handling, storage and transportation. The diametrical pressure force differs according to the variants and their mixtures, correlating with the abrasion values (see chapter 3). The lower the abrasion values, the higher are the strength forces which the agglomerates can withstand.

Figure 76 displays the results in two different y-axis scales, which are 0 N to 200 N and 0 N to 10000 N. The two different scales are chosen based on the obtained results. The build-up agglomerates result in lower strength withstanding capacities in comparison to that of encapsulated and press agglomerates.

It is found from this work that the C-types (C1, C2) of agglomerates can withstand higher forces compared to that of L-types (lime), S-types (starch), G-types (gelatin), CMC types, alginate capsules, lignin granules and PLA agglomerates. The encapsulation of build-up agglomerates with alginate (AL-S, AL-G, AL-CMC) increase their strength resistivity. The withstanding forces of the produced agglomerate variants are in the order of centrifuge (C1, C2) > AL-CMC > CMC > AL-S > starch (S) > AL-G > gelatin (G) > lime (L1-L6) > lime (L7-L12) > gelatin capsules (GC) > PLA > alginate liquid capsules (AL1).

The centrifuged agglomerate variant C2 comminuted with 6 mm sieve aperture size has higher pressure withstanding capacity (9800 N) in comparison to that of C1 (9214 N) comminuted with 10 mm sieve aperture size, indicating better press agglomeration characteristics with respect to the lower particle sizes. Similarly the variants L1 to L6 show better strength characteristics compared to the variants L7 to L12. L3, L7 variants in the groups L1-L6 and L7-L12 display the highest withstanding forces (20 N and 17 N respectively) among the build-up agglomerates with the additive lime.

The variants S2 (25 N) and AL-S3 (49 N) in the groups starch (S1-S3) and alginate starch capsules (AL-S1 to AL-S3) display high force resistivity with the binder starch. The variants G3 (13.9 N) and AL-G2 (24 N) display higher strength resistivity with the binder gelatin. CMC3 (92 N) and AL-CMC3 (154 N) display the highest force resistivity characteristics in comparison to all the other binders. GC1 has higher strength resistivity compared to GC2. The liquid capsules (AL1: 4 N) and PLA (3.8 N) capsules result in the lowest strength resistivity in comparison to all the other variants. The gelatin capsules (GC3) produced with 50 % GC2 and 50 % AL1 together result in an increase in strength bearing capacity from 4 N to 8 N.

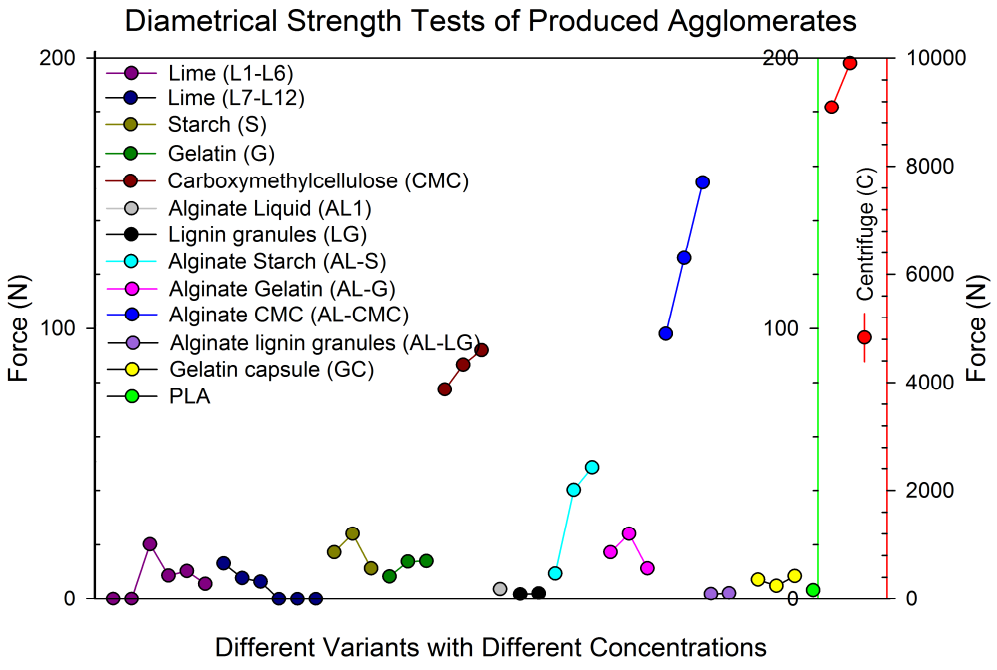


Figure 76: Diametrical strength test of biogas residues pellets of different variants.

The agglomerates produced (build-up, press and encapsulation) with 6 mm comminuted residues display better abrasion and strength results compared to those of the 10 mm comminuted residues. This is due to the reason that 6 mm fibres have lower stiffness and smaller particle sizes compared to 10 mm fibres. The particle size influences the binding properties of the particles in agglomerates.

The formation of agglomerates is also influenced by the fibre particle sizes. Smaller fibres increase the contact points between the other fibres and the additive mixture materials influencing the formation of stable agglomerates due to a higher number of contact points between the particles. This also results in the formation of high durable agglomerates with high strength resistivity and low abrasion values.

The percentage of additive lime required is high and ranging between 40 wt. % and 50 wt. % compared to the binders. The binders result in lower amount requirements ranging from 2.5 wt. % to 20 wt. %. Especially the binder CMC results in best results such as low abrasion values, high strength resistivity with low amounts ranging from 2.5 wt. % to 10 wt. %. The encapsulation of CMC with alginate has further increased the stability of the produced agglomerates.

The results from the abrasion tests show a correlation to the strength results. The pellets with minimum abrasion values (L3, L7-L9, S5, G5, CMC3, C2 and GC1) result to have high strength resistance values (see also chapter 3).

Further the **chemical analysis** (total nitrogen and ammonium contents) of the produced agglomerates are carried out to verify the changes depending on the additives, binders and the encapsulation processes in comparison to those of the conventionally produced press agglomerates (table 14).

The press agglomerates C1 and C2 show high containment of nitrogen (85 % to 95 %) but very low containment of NH_4 (8.5 % to 9.4 %). The results from press agglomerates indicate a high loss of ammonium contents (90.6 % to 91.5 %) as ammonium is mainly present in the liquid phase and is separated in the conventional process by undergoing solid-liquid separation before the agglomeration process.

The build-up agglomerates produced with lime show high reduction in both nitrogen and ammonium contents ranging from 85 % to 96 % and from 95 % to 98 % respectively. This decrease in nitrogen and ammonium contents can be due to the high amount of additives requirement in the agglomeration process changing the proportions of the components.

The build-up agglomerates produced with binders show better results compared to those with the additives. The variants produced with the binder starch (Nitrogen: 34 % to 41 %; NH_4: 70 % to 84 %) and binder CMC (Nitrogen: 28 % to 43 %; NH_4: 39 % to 51 %) show that they can retain major proportions of nitrogen (up to 43 %) and NH_4 (up to 84 %), indicating that these agglomerates are more efficient in their utilization as fertilizers in comparison to the centrifuged variants and additive lime variants. The binder gelatin results in highest containment of nitrogen and NH_4. This increase is due to the high presence of nitrogen (up to 18 %) and NH_4 (up to 0.25 %) in gelatin (Eastoe and Leach, 1958; www.gelatin.co.za, last visited on 12.09.2012). Even though gelatin build-up agglomerates do not show stability, they showed high retainment of nutrients useful as fertilizer.

Table 14: Nitrogen and ammonium contents of the produced agglomerates.

Variants		Nitrogen and Ammonium Contents		Products
		N g/kg TS	NH_4 g/kg TS	
Biogas Residues		18.400	1.060	
Additive	L1	2.280	0.043	Product 3
	L2	2.110	0.036	
	L3	1.130	0.031	
	L4	1.710	0.022	
	L5	1.810	0.018	
	L6	0.830	0.031	
	L7	2.830	0.034	
	L8	2.100	0.038	
	L9	1.150	0.027	
	L10	1.310	0.024	
	L11	0.950	0.041	
	L12	0.720	0.019	
Binders	S1	7.510	0.890	Product 3
	S2	7.280	0.840	
	S3	6.360	0.738	
	G1	18.040	1.016	
	G2	17.710	1.024	
	G3	17.340	0.902	
	CMC1	7.890	0.540	
	CMC2	6.230	0.435	
	CMC3	5.210	0.410	
Encapsulation	AL1	3.920	0.810	Product 5
	LG1	2.740	0.660	
	LG2	3.450	0.790	
	AL-S1	7.660	0.980	Product 4
	AL-S2	7.430	0.930	
	AL-S3	6.510	0.825	
	AL-G1	18.190	0.978	
	AL-G2	17.860	0.894	
	AL-G3	17.490	0.811	
	AL-CMC1	7.980	0.630	
	AL-CMC2	6.320	0.525	
	AL-CMC3	5.300	0.500	
	AL-LG1	2.840	0.690	
	AL-LG2	3.520	0.850	
	GC1	18.180	1.025	Product 2
	GC2	18.360	1.041	
	GC3	18.130	1.020	
	PLA	17.560	0.954	
Cent	C1	15.550	0.100	Product 1
	C2	16.430	0.090	

The encapsulations of the binder build-up agglomerates with alginate result in a slight increase in nitrogen and ammonium contents compared to those of the binders alone. This increase is due to the low amounts of nitrogen and NH_4 contents present in alginate (0.09 % to 0.17 %).

The retainment of nitrogen and NH_4 in agglomerates produced with the different binders in comparison to that of the centrifuged agglomerates is due to binding of both the solid and liquid phases together. The reduction of nitrogen and NH_4 contents compared to direct residues is due to the desiccation of liquids through the surface of agglomerates and is also due to the changes in mix proportions with binders.

The direct encapsulation of biogas residues with gelatin capsules (GC) and polylactic acid foils (PLA) result in the almost 100 % retainment of nitrogen and ammonium contents. A decrease (4 %) in these contents is observed with PLA, which is due to the PLA material proportional substitution as encapsulating material.

The direct encapsulation of the liquids with alginate resulted in higher retainment of nitrogen and NH_4. The encapsulation of liquids with lignin granules resulted in a slight reduction of nitrogen and NH_4. The liquid encapsulated lignin granules with their controlled release (see chapter 4) can be easily adapted in to the existing systems and are more advantageous as they reduce the risk of groundwater and water bodies contamination.

6. Comparison of conventional and innovative processes

This chapter compares the conventional and innovative processes presented in this thesis directly with each other. Through this comparison the innovation of the processes and the refinement of thus produced multipurpose end-products shall be highlighted.

6.1 Agricultural residues

Agricultural residues (straws, shells, husks, etc) are presently playing important roles due to their possible substitution of fossil resources. Biomass wood resources are acting as promising alternative biogenous resources useful for material as well as energetic applications. Agricultural residues are gaining more importance at present due to their yearly availability and they are also considered as environment friendly bio-fuels (CO_2 neutral).

Conventionally straws are baled in a semi-dry state directly at the field with the help of heavy agricultural machinery. Baling is carried out in a fully automated process and increases the density of straws from 40 kg m^{-3} to 180 kg m^{-3}. The production of straw bales also increases the ease of straw logistics in handling, transport, storage, etc.

The density of straw is increased by baling compared to that of loose straws, but the obtained bale density is still very low. The moisture content of the straws in bales can lead to the formation of mold (fungi), negatively affecting the quality of the material and its further usage. Straw bales often contain impurities such as metals (from field work), sand, etc.

The direct combustion of straws / baled straws impose some problems as there is a risk of high emissions formation in combustion due to high sulphur content, boiler scaling or corrosion due to high chlorine content and formation of slagging due to non-uniform combustion. The non-uniform combustion is due to the differences in oxygen supply dependent on the hollow structure of the straw.

The production of cereal straw press agglomerates is an innovative processing and refinement method having definite advantages over the conventionally used straw bales for the energetic as well as material applications. The density of straw is increased from 40 kg m^{-3} to approx. 540 kg m^{-3} with the help of a press agglomeration process improving transport, handling and storage. Agglomeration also improves the energy density of straws and reduces the slagging effect during combustion due to the uniform combustion behaviour of densified pellets. The press agglomerates also reduce the logistic costs for handling, transport and storage due to their high density and high durability.

The production of cereal straw press agglomerates requires more process steps in comparison to that of the straw bales such as the produced bales have to be transported to the agglomeration plant and have to undergo additional process steps such as comminution, homogenisation, press-agglomeration, conditioning, etc.

The increased process steps increase the energy need of the process. In comparison to wood press-agglomerates undergoing the same process steps, straw press-agglomerates have relatively low energy. Even though the straw press-agglomerates are better in handling compared to straw bales, they still have high sulphur and chlorine contents creating problems in emissions and corrosion of the boilers. These problems with the high sulphur and chlorine contents can be solved with the help of a refinement process by using suitable additives, binders, etc. reducing their negative effects.

The refinement of straw press-agglomerates through innovative processing is achieved with the help of biogenous and fossil fuel additives (see chapter 3). The produced biomass mix agglomerates have energy values equal to those of wood agglomerates. The refined straw press-agglomerates produced with additives have advantages such as increased density, high durability, low sulphur, low chlorine, etc. compared to those prepared without additives. Further the produced biomass mix pellets can easily substitute the biogenous wood as well as fossil fuels.

6.2 Industrial residues

Black liquors are residues from the industrial pulping processes for the production of pulp and paper. The most common used pulping processes are sulphite and sulphate pulping processes (see chapter 2).

After pulping, the pulping residues can be treated to separate the lignin from black liquors. This separation of lignin is mainly carried out with the help of a liquid liquor acidification process using CO_2 and H_2SO_4 (see chapter 2) acids. This liquid liquor acidification separation process is considered to be the conventional process and is compared with the patented innovative and refinement process.

The conventional process provides a method for the separation of lignin from black liquor using an acidification process and comprises of four processing steps starting with precipitation and ending with the agglomeration of lignin (see chapter 2). The patented innovative and refinement process set-up is completely converse to the one used in the conventional process, starting with the agglomeration (spray granulation) of the black liquors (figure 77) and then treating the granules with acids (H_2SO_4, CH_3COOH).

The advantage of starting the separation process with the production of granules lies within the size of the thereof produced granules. The granules have a high surface area making them more suitable for the reaction with acids, which will be added in the consecutive acidification process step. The acidification leads into the modification of the lignin structure back into its original hydrophobic form. The acid treatment is more efficient and faster to that of the conventional process due to the high surface area of the granules.

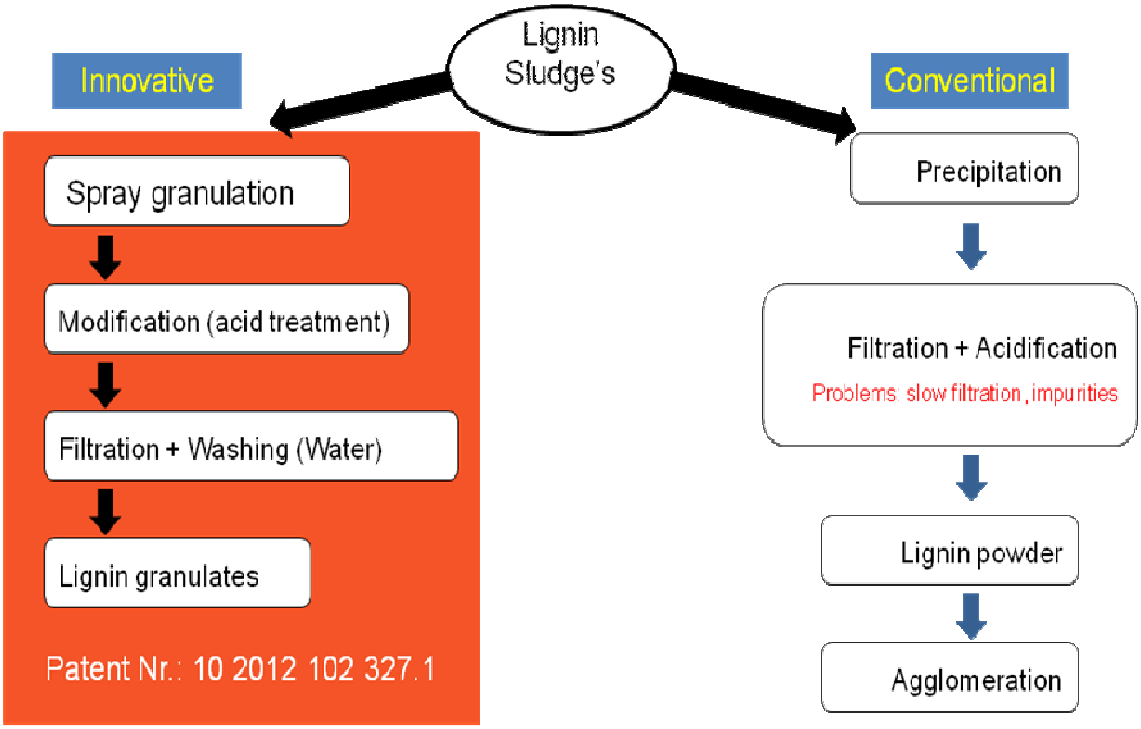


Figure 77: Comparison of process steps of the innovative patented process and the conventional processes.

In both the conventional process and the patented innovative and refinement process the subsequent process step after the acidification is the filtration. The conventional process substantiates problems in the filtration due to the fine dust / colloid particle sizes (5 to 40 µm) of lignin along with the impurities adhering to the lignin (Theliander and Ohman, 2006). The granules from the patented innovative and refinement process retaining their structure avoid / reduce the formation of fine dust / colloid size particles and simultaneously increasing the filtration efficiency. The granule structure makes the filtration process easier and more efficient.

The conventional process produces lignin cake as end product with 30 wt. % moisture content (Ohman et al., 2006), which is then dried, comminuted to powder and densified with pressure into agglomerates to avoid the risks (explosion) with powder handling (see chapter 4). Dry lignin powder has a high explosion risk and needs to be agglomerated in a fourth process step in order to reduce this risk. The end products of the conventional process are lignin press-agglomerates.

After the filtration and washing process step in the patented innovative and refinement process, the end products are process integrated lignin agglomerates (granules). These do not necessarily require further processing as they do not impose explosion risks (see chapter 4). By a voluntary briquettisation process, the granules (then briquettes) have attained a higher energy density, and the briquettes are better to store, handle and transport.

The produced briquettes further reduce the development of fine dust particles due to the enclosement of them in between the inter-space of the granules. This enclosement of the fine dust particles in the briquettisation process also result in an increase in impurities measured with increasing sulphur and ash contents in comparison to that of the granules.

The negative aspects of the patented innovative and refinement process is the energy requirement of the spray granulation process (single evaporator). A positive energy balance of the total process energy can be achieved when the throughput of granules from the spray granulator is more than or equal to that of one kilogram per hour. The calculated energy requirement and material throughputs are only based on the data obtained on a laboratory scale. This innovative process can be integrated easily in the pulp industries reducing the number of evaporator's usage in comparison to that of conventional process (3 early and 3 late evaporators).

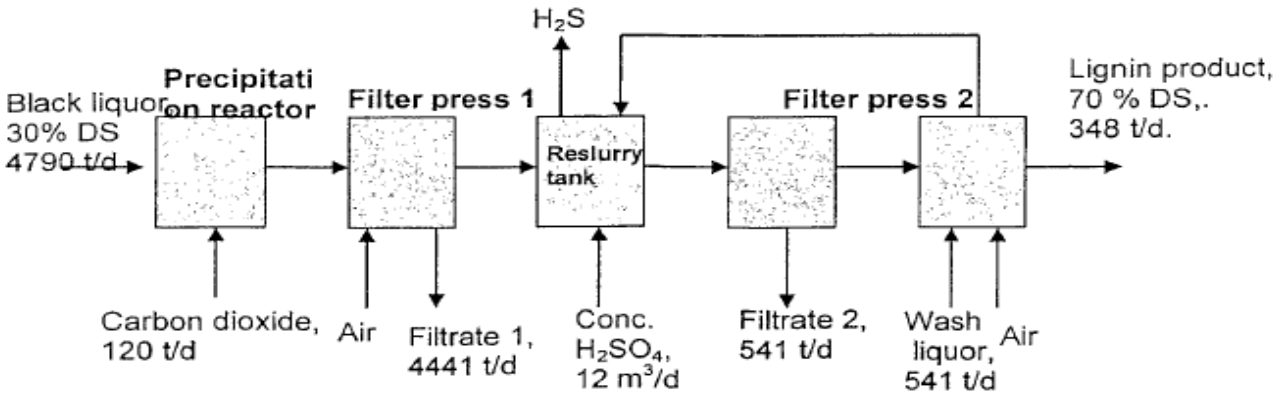
The energy requirements of the conventional process are not completely known as it usually uses the energy produced in the pulp and paper industry directly. With two or more evaporators included in the process it is not estimated to perform better than the patented innovative and refinement process.

Further the material flow patterns of the conventional process are compared with the new innovative patented process in figure 78. The material flow patterns of the conventional process are displayed in figure 78a consisting of five process steps which are closely described in chapter 2. The material flow patterns of the innovative patented processes are displayed in figures 78b (Kraft liquor) and figure 78c (Ca-LS, Na-LS) and are closely described in chapter 4. The material amounts in figure 78c are represented with green colour for Ca-LS and in blue colour for Na-LS.

The material flow patterns of the conventional process and the innovative patented process (figure 78) are quite similar on a first glance. The main difference between the processes is the formation of structural integrated lignin agglomerates (granules / briquettes) in the innovative process. In comparison to the innovative process, the conventional process obtains a lignin cake with 30 wt. % moisture content. The production of lignin agglomerates in the first steps of the innovative process resulted in higher yield of lignin compared to the conventional process.

Further processing of these agglomerates is not necessary in comparison to the conventional process where an additional agglomeration process step is obligatory to reduce explosion risks and to ease the handling, storage and transportation.

a)



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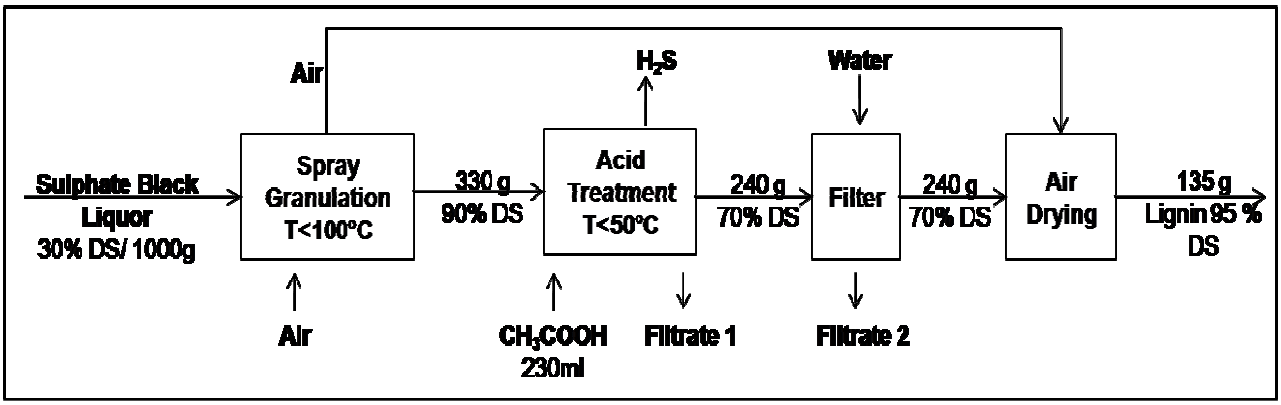

c)

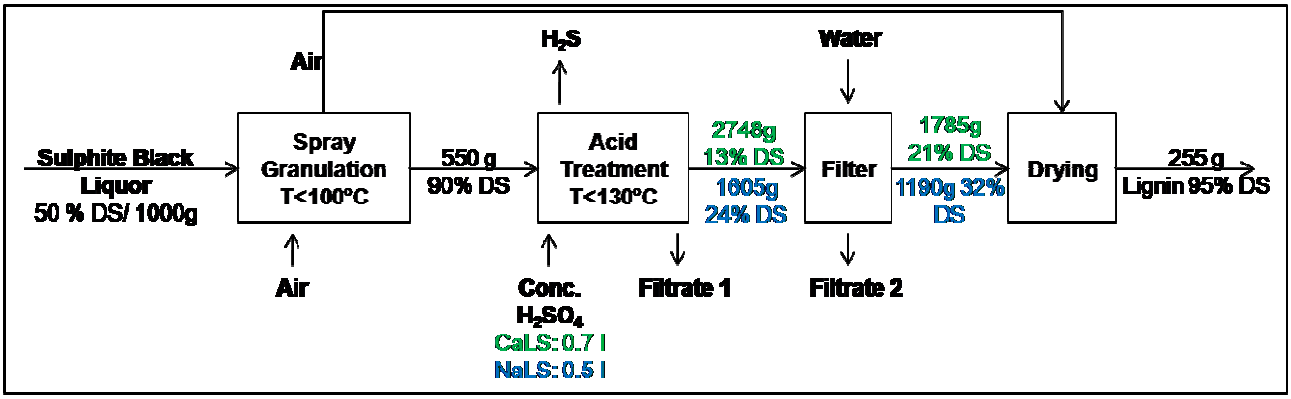

Figure 78: Material flow patterns of the (a) conventional process (Ohman et al., 2006) and (b and c) innovative patented process.

6.3 Biotechnological residues

Biotechnological (biogas) residues are either of liquid-liquid or solid-liquid mixtures with moisture contents ranging from 80 wt. % to 85 wt. %. These residues can be stored as liquids and can be used as liquid fertilizers in the conventional process. The high liquid content of the biogas residues imposes problems for the producer concerning the handling, storage and transportation logistics. The most common utilization of these residues is as liquid fertilizer in the fields.

Fertilization with biogas residues is only allowed in particular defined times of the year due to regulations. Transport of liquid residues is only profitable over short distances (< 35 km). Liquid biogas residues also create problems with groundwater and water-bodies contamination as the directly sprinkled liquid percolates faster in the field than dry fertilizers.

The conventional processes solving the storage and handling problems of the residues undergo solid-liquid separation and agglomeration of the solid residues. The negative aspect of this process is a reduced fertilizer efficiency of the solid residue agglomerate by around 54 % of total nitrogen, with 47 % reduction of ammonium, 60 % reduction of phosphorus and 48 % reduction of potassium contents, which are mainly concentrated in the liquid phase. The sprinkling of separated liquids results in high nitrate accumulation in ground water and water bodies. This high nitrate contaminates them due to faster percolation and leaching effects. The conventional agglomeration of solid phases also produces laughing gas emissions as press agglomeration pellets are generally produced at temperatures higher than 50 °C.

The refined encapsulation process produces biogas residue agglomerates which are able to contain / hold both the solid as well as the liquid phases of the biogas residues together. Through which most of the problems, occurring with liquid biogas residues or the conventional biogas residue agglomerates, could be solved.

The patented innovative biogas residue agglomerates improve the handling, storage and transportation as well as odor problems of liquid biogas residues, by giving the residues a defined durability and strength similar to that of the conventionally produced biogas residue pellets. However the conventional biogas residue agglomerates loose the fertilization efficiency due to the separation of solid and liquid phases. The innovative biogas residue agglomerates encapsulate the liquid state of the biogas residues, keeping the highly nutritious fertilization effect (see chapter 5). The encapsulation of the liquid and solid phases together guarantees a controlled release of the fertilizing nutrients, which can help improving soil qualities and will not negatively affect ground water and water-bodies contamination.

Compared to the direct usage and even the production of conventional biogas residue agglomerates, the process steps of the innovative biogas residue pellets are more cost and energy intensive, but the end product is a valuable fertilizer which can be made marketable. This option is not given for the marketability for liquid biogas residues, and also not for the fertilizer of the conventional biogas residue pellets.

Further this patented innovative process uses a minimum number of processing steps and can be carried out either in direct encapsulation or indirect encapsulation processes. The direct encapsulation with minimum processing steps reduces laughing gas emissions in comparison to that of the conventional production process.

7. Conclusion

This thesis tries to optimize conventionally applied processes, which are only successful to solve certain challenges in handling of biogenous residues such as agricultural, industrial and biotechnological residues. This work develops new innovative agglomeration processes optimizing the conventional processes and simultaneously solving more challenges and handling problems.

The innovative process steps are constituted in such a way that desired properties of the end products can be achieved efficiently. This work tries a new approach in processing and handling the different residues in comparison to the conventionally used processes.

The developed three different processes dealing with agricultural, industrial and biotechnological residues use a new and innovative agglomeration process and try to optimize the production process to produce desired multipurpose end products. The innovative processes and the obtained end products have resulted in an optimized, sustainable and environmental friendly utilization of biogenous residues. This further results in the value addition of the biogenous residues, which are till now considered as low value materials.

7.1 Agricultural residues

The end moisture content of the cereal straw pellets (see chapter 3) measured after stabilization is below 10 wt. %, through which the pellets can be stored for longer time periods. Particle size characteristics of the cereal straws showed a good correlation to the abrasion values of the thereof produced pellets. Particle size distribution also shows favorable characteristics for the combustion processes in furnaces. Minimum abrasion values are obtained from the pellets prepared with 17 wt. % water content (rye straw, P1, P2 and AC) and 18 wt. % water content (wheat straw, LC1 and LC2). The pressure tests also show a good correlation with the abrasion values. The biomass blend pellets with additives display low abrasion and high strength withstanding characteristics.

Abrasion of pellets is one of the most important mechanical parameters. The abrasion results show a positive correlation between time and abrasion, which are investigated with the help of two different tumbling devices. The tumbling device SS 187120 displays lower abrasion compared to the tumbling device ASAE S 269.4. This lower abrasion values from SS 187120 are due to the shape of the tumbling device. A correlation exists between both the abrasion testing devices. The abrasion values obtained with the tumbling device SS 187120 increase with increasing number of baffles. The increase in abrasion with a higher number of baffles is due to the higher number of encounters undergone by the pellets in between the walls of device and the installed baffles in comparison to the tumbling device without baffles.

The measurement of abrasion gives only information on the mechanical stability of the pellets against a certain number of encounters in a particular time limit (10 min). Even though these abrasion values indicate the pellets stability, they cannot be transmitted 100 % to the industrial scale produced pellets as the industrial scale pellets are transported, stored and handled in big amounts with hydraulic and mechanical automated feed pumping systems. The industrial scale handling of pellets results in higher number of encounters, resulting in higher abrasion. The tumbling device ASAE S 269.4 simulates a higher wear and tear stress on each pellet than SS 187120, giving a more precise picture on the real abrasion values. A possible way to make the tumbling device SS 187120 more precise (equal to ASAE S 269.4) is to install more number of baffles, increasing the number of pellet encounters.

In order to define the stability of the pellets after various handling stages such as transportation and storage, abrasion as a single mechanical stability parameter is not sufficient. Therefore strength of pellets has to be taken into consideration as a supporting parameter along with the abrasion. Strength parameters such as three points bending, point bending, diametrical force and impact resistance force are investigated. The abrasion values and strength results of the pellets show positive (diametrical, three point, point and impact resistance) correlations. The strength measurement simulates at the highest pressure, which can occur on any pellet in any position of a batch of pellets.

The positive correlations between abrasion and strength can be related to the direction principle of forces acting on the pellets under different strength and abrasion tests. The positive correlation indicates that for the quality assurance of pellets one more testing parameter, namely strength, has to be provided to the producer and consumer together with the parameter of abrasion, as abrasion as quality parameter alone is not sufficient to simulate the genuine wear and tear stresses on every pellet. The additional strength parameter along with the abrasion parameter would increase the reliability of the data especially on the quality of the pellets.

Regarding the CO_2 emissions, combustion of straws is considered CO_2-neutral, but the calorific value and the bulk density of straw are low compared to that of woody biomass. Therefore rye and wheat straws can be used as energy sources after densification in the form of pellets, which have high density (> 540 kg m^{-3}) and comparatively high heating values of 17.2 MJ kg^{-1} and 17.4 MJ kg^{-1} respectively. The heating value of the straws is increased with the addition of biogenous and fossil fuel additives. The biogenous and fossil fuel additives have enhanced the heating values from 17.2 MJ kg^{-1} to 18.5 MJ kg^{-1}, with a simultaneous increase in the density (from 540 kg m^{-3} to 670 kg m^{-3}) of the straw pellets. The production of BMPs and the enhancement of their heating values increase the added value of the agricultural residues (straws) as solid bio-fuels, substituting fossil fuels as well as wood fuel resources. The produced straw-additive pellets (BMPs) can compete with fossil fuels as well as with the conventionally produced wood pellets concerning their individual heating values in their utilization. With a heating potential similar to that of wood pellets, a wide ranged utilization of straw-mix pellets can be achieved.

The most suitable biomass (mix) pellet is obtained by considering different investigated parameter results in order of their importance over the quality of produced pellet variants. The considered parameters are in the following order: (i) particle size distribution, (ii) chemical properties (S and Cl), (iii) lower heating value, (iv) abrasion and (v) strength. 17 wt. % to 18 wt. % water content of the biomass mixtures result in good pellet qualities and the produced pellets with these water contents are only compared.

The particle size distributions (figure 38) show that the material mixture AC, followed by LC1, LC2 and RS HM have the most favorable particle size distribution, with a high amount of fines and a comparatively high amount of long fibres. This distribution is preferred during pelletisation as the binding forces of the pellets with this particle size distribution are highest.

Small particle sizes are preferred during combustion due to their low thermal thickness, which benefits the incineration process. Among the produced BMPs, the pellet variants LC1 and LC2 display lower abrasion and high strength characteristics. This low abrasion and high strength are due to high binding effects of the particles, retaining their structure even after a high number of encounter impacts.

The sulphur content in the wheat and rye straw materials show the lowest amounts with 0,082 and 0,085 % of dry mass, followed by P1, P2, LC1 and LC2 (0,09 – 0,16 %). The chlorine content in the mixtures P1, P2 and LC1 are lowest followed by LC2 and AC. The wheat and rye straws display high chlorine contents. The chemical properties (low sulphur, low chlorine and low ash contents) of the BMP variants P1 and P2 display the most favorable overall chemical characteristics followed by LC1 and LC2.

Lowest abrasion values are obtained from LC2 pellet variants (figure 42). Both LC1 and LC2 excel as the pellets with highest strength (figure 44) among the different produced variants with the investigated three different strength tests. Abrasion values for P1 and P2 are very high. The additives palmitin and paraffin are waxes, which are chosen due to their ability to increase the heating value with low amounts of addition and also the ability to ease the pelletisation process when heated. Once the pellets are cold, they tend to be brittle and therefore result in high abrasion and low strength values. The biomass mix pellets P1 and P2 excel with their high heating values along with their comparatively good chemical properties making them suitable as better fuels. The only problem in their usage as pellet fuel is the low mechanical stability (high abrasion and low strength).

The biomass-lignite mixture pellets (LC1 and LC2) result as the best fuel pellets throughout the produced BMP variants compared with the help of various parameters (physical and chemical). The produced AC pellet variant (12.16 wt. % anthracite coal) display a better particle size distribution and similar heating value as the pellets with LC2 having 21 wt. %, but display only mediocre abrasion and strength values, have a high content of sulphur and medium content of chlorine.

The rye and wheat straw pellets have the lowest heating values, but comparatively good abrasion and strength values (RS EX). They have the lowest sulphur and highest chlorine contents.

The biomass-mix pellets with lignite (LC1 and LC2) are very well suited for big scale production as they are highly resistant to mechanical stresses and have a heating value equal to that of wood pellets. Due to the negative effects in boilers as indicated by the chemical compositions, they should only be applied in industrial power plants, e.g. in co-combustion along with fossil fuel coal in power plants. The pellets produced with agricultural residue rye straw with an admixture of 21 wt. % lignite (LC2), indicate that the rye straw can be easily used as a biogenous additive in lignite incinerating industrial power plants.

The preparation of straw pellets and increasing the heating value of straw pellets with biogenous and fossil fuel additives are economical and ecological way towards the transition to the generation of residue biomass energy. This approach uses existing power plant equipment without any major modifications, making the process of transition more economical.

The main drawbacks of the agricultural residues (straw) in energy applications are high dust production, huge amount of ash formation and high emissions. The straw incineration results in high NOx emissions and also causes depositions and corrosion of the furnace due to high presence of S and Cl. Special furnaces with filters have to be used especially when straw is to be incinerated. The direct combustion of straw is profitable in full scale power plants. The produced BMPs have displayed better incineration properties compared to the traditional incineration of straw bales.

7.2 Industrial residues

The challenging / restricting issues in utilization of lignin sludge's (black liquors) are the high moisture content, presence of harmful cooking chemicals, high reactivity in powder form, high sulphur emissions, etc. The utilization of lignin sludge is restricted mainly due to the high presence of cooking chemicals and sulphur content. Special filters have to be used especially in the combustion of lignin sludge's. The combustion of lignin sludge is mainly profitable in full scale power plants. The combustion of lignin sludge's is considered to be CO_2-neutral as it is originating from the biogenous raw material wood and is treated as biogenous industrial residue. The disadvantage in the handling and combustion of lignin sludge is the high amount of water content, which is reducing the calorific value of the material due to evaporation losses (see chapter 2). The calorific value of lignin sludge can be increased by producing agglomerates (granules / briquettes).

The granules of lignin sludge's are produced with the help of a spray-drying / spray-granulation process, which increases the calorific value of the end products (hydrophobic granules) on average from 10 MJ kg^{-1} to a value in between 25 MJ kg^{-1} and 33 MJ kg^{-1} depending on black liquor characteristics and their treatment processes.

The density of the produced spray dried granules reduces with increasing temperatures. The produced granules still contained impurities (cooking chemicals, sulphur) and are either hydrophilic (ex. Ca-LS and Na-LS) or hygroscopic (ex. KL). The impurities from granules are cleaned with the help of an acid treatment (H_2SO_4 / CH_3COOH). The acid treatment is only investigated with the granules having higher density compared to that of lignin powder.

The acid treatment results in the removal of the impurities and sustaining the structure of the granules as particles. The granules in the acid treatment have undergone a structural modification due to the melting and bridging of particles in the granule. The melting and bridging lead to encapsulation of the granules and is dependent on the porosity of the granules. The encapsulated lignin granules are insoluble in water by regaining the lignin's basic insoluble characteristic before the pulp cooking process. The encapsulated granules simultaneously improve the filtration efficiency.

The acid treatment of granules in a volume restrained device result in the development of briquettes. Briquettes further increase the density of the granules. The production of briquettes is carried out by melting and bridging of the particles inside the granules and with the neighbouring granules. Briquettes increase the filtration efficiency further compared to that of the granules. The increment in filtration efficiency of the briquette is due to enclosement of colloidal or fine dust size particles between the granules in the development of briquette.

The impurities of the granules or briquettes are measured with respect to their sulphur and ash contents. The granules show a reduction in sulphur (7.3 % to 2.7 %) and ash contents from 13.5 % to 3.9 % and 44.37 % to 0.58 % after the acid treatment respectively, which indicates the removal of impurities along with the stabilization of granule structure. The briquettes produced from calcium lignin sulphonate and sodium lignin sulphonate result in higher sulphur and ash contents. These increments are due to the containment of acids and cooking chemicals inside. Even though the briquette produced from Kraft lignin show a reduction in sulphur (from 7.35 % to 5.93 %) and ash contents (44.37 % to 41.30 %), they are not significant and they still contain impurities compared to the granules.

The production of granules or briquettes following an acid treatment is considered a more economical as well as ecological way of lignin sludge treatment compared to the direct combustion of lignin sludge's. This is due to their (i) increased filtration efficiency, (ii) reduction in acid requirement compared to traditional flocculation systems, (iii) regaining its original insoluble characteristic, (iv) increase in calorific value, (v) impurities reduction and (vi) reduced handling and maintenance costs. This process is presently only tested on laboratory scale and it is expected that it can be implemented easily in the existing paper and pulp industries without major modifications, making the process more economical, ecological and environmental friendly.

7. Conclusion

The integrated agglomerate production process of the innovative patented process can produce a variety of products ranging from agglomerates (granules / briquettes) to biodegradable acid stable micro-porous membranes with slight modifications in the process. The production of such variety of products in the conventional process has to be carried out individually for each product. The production of integrated multipurpose end-products achieved with only slight modifications makes the process more application friendly and sustainable.

The production of such biodegradable acid stable micro-porous membranes is so far only carried out on the base of fossil raw materials. Production of such membranes from the biopolymer lignin increases the added value of the lignin as well as of the biogenous residues and broadens their application possibilities.

Compared to the conventional processes in separating lignin from black liquors and producing agglomerates (pellets), the innovative patented process described in this thesis has the following advantages: (i) production of process integrated hydrophobic agglomerates (granules / briquettes) reducing the need for further agglomeration, (ii) more efficient and faster acid treatment due to the size and surface area of the produced granules, (ii) reduced filtration problems due to particle size of the granules, (iii) higher yield of lignin with high purity.

The disadvantage of the innovative patented process is the requirement of high amounts of acids in comparison to the conventional separation process, which is needed due to the increased surface area of the granules. The innovative process compensates this high acid requirement with the high yield of lignin compared to the lignin yields of conventional processes. Even though the new innovative process requires high amounts of acids, when compared to the yield of both the conventional and innovative processes, the acid requirement is almost similar.

The production of process integrated briquettes is another option in the innovated patented process. The briquettes contain a higher amount of impurities than the process integrated granules and have a lower heating value (Ca-LS: 19.48 MJ kg^{-1}; Na-LS: 21.37 MJ kg^{-1}; KL: 23.41 MJ kg^{-1}) than that of the granules (Ca-LS: 26.59 MJ kg^{-1}; Na-LS: 25.30 MJ kg^{-1}; KL: 33.19 MJ kg^{-1}) (table 11 and 12). The lower heating value of the briquettes is still higher than that of the direct incineration of black liquors (9 – 17 MJ kg^{-1}) as well as of wood (17.5 – 19.5 MJ kg^{-1}). Lignin briquettes can be used as multipurpose products. They do not only function as renewable fuel, but can also be used as catalysators due to its porosity and can also be used in the separation of cat ions due to the retainment of acids (Kurth et al., 2006).

Due to the high heating values of the agglomerates (granules and briquettes), combustion in common small scale boilers may not be possible. Common small scale boilers are usually equipped to combust wood, but are not suitable for materials with higher heating values as they are produced per the standards specified. Increased heat could lead to a deformation of the boilers. Direct combustion of the produced lignin granules should only be carried out in big scale combustion units.

A combined combustion with lignin granules and other biogenous residue materials (straw, biogas residues, etc.) in the form of biomass mix pellets could be an option for usage in common small scale boilers. The high sulphur, chlorine and ash contents of the biogenous residue materials can be compensated by producing BMPs with the admixture of lignin granules simultaneously increasing their heating values equal to that of wood. The BMPs can act as new renewable fuels for energetic usage in small scale boilers.

The most advantageous agglomerates produced with the innovative patented process are the lignin granules. The produced lignin granules display high lignin purity. Further based on their particle sizes they can be easily integrated in different processes in the production of multipurpose products, which can be applied either in energetic or material applications.

The innovative patented process optimizes the process of using lignin sludge's and proves to be superior to the conventional lignin handling process on lab scale.

7.3 Biotechnological residues

In the conventional handling of biogas residues the solid and liquid phase of biogas residues are separated. Agglomerates or pellets are produced from the solid phase and the liquid phase is either brought to field separately as liquid fertilizer or is treated such that the effluents can be discharged into water bodies.

The fertilizing effects of biogas residues are reduced with the separation of solid and liquid phases, which is due to the separation of nitrogen and ammonium contents mainly concentrated in the liquid phase. The conventionally produced agglomerates are containing only low amounts of the original nitrogen and ammonium contents. Further the pellets or agglomerates disintegration and degradation in the soils also requires time and through this, the effectiveness of biogas residues as fertilizers is reduced.

To overcome these problems, this work utilizes encapsulation technologies and tries to hold both the liquid and solid phases together in the agglomerates. The pathways of the encapsulation technologies are chosen in such a way that only slight modifications of conventional processes are required and can be easily integrated into existing processes.

Agglomerates are produced i) with the solid phase materials after dewatering and separating liquids (C1, C2), ii) with different additives (L1 to L6, L7 to L12) and iii) with different binders (S1 to S3, G1 to G3 and CMC1 to CMC3). The binders and additives are chosen in such a way that they can effectively bind both solid and liquid phases together. Further direct (AL1, GC1 to GC2, PLA) and indirect (AL-S1 to AL-S3, AL-G1 to AL-G3, AL-CMC1 to AL-CMC3) encapsulation of biogas residues is carried out. The results show that the biogas residue mixture L3 (54 wt. %) and L7 (50 wt. %) to L9 (54 wt. %) are optimal in producing agglomerates with pelleting discs due to their high strength and low abrasion values in the variants group additives. The 50 wt. % to 54 wt. % lime mixture is too high and is not economical.

The agglomerates produced with the help of binders show better results (both strength and abrasion) in comparison to that of the agglomerates produced with additives. The amount of binders (2.5 wt. % to 20 wt. %) required in build-up agglomeration process producing agglomerates is low compared to that of the additive amounts (50 wt. % to 54 wt. %).

The press pelletisation of the residues is carried out without additives. The liquid phase is separated with the help of centrifugal force. About 75 wt. % of the water can be removed from this process and the dewatering efficiency reduces (from 85 % to 35 %) with reducing particle sizes (measured with 10 mm and 6 mm classifier sieves). The pellets from press pelleting (C1, C2) have a greater force resistance and lower abrasion values as compared to the other types of agglomerates produced.

The produced capsules from PLA and GC result in low abrasion and low strength characteristics. The low strength is due to the bursting of the enclosed PLA foil with pressure; whereas the low strength of GC is due to the brittleness of GC in dry state.

The produced agglomerates show a reduction in nitrogen and ammonium contents (with additives, with binders, after dewatering), which indicates a decrement in fertilizer efficiency of the residues. The highest reduction is observed with the agglomerates produced after dewatering (C1, C2). The binders show comparatively better results in holding nitrogen and ammonium contents (up to 60 %) in the agglomerates, indicating a better fertilization effect compared to that of the conventionally produced pellets. The results show that the binder CMC is the best among the investigated binders and additives. The amount of CMC required is minimum (2.5 wt. %) compared to others. The CMC produced agglomerates are highly stable and increased the fertilizing efficiency to 50 % compared to the fertilizing efficiency of conventionally produced pellets. The main reasons for observed increase in nitrogen and ammonium contents are due to the treatment process running at temperatures below 50 °C and simultaneous binding of liquids with solid phases together.

The water content in the agglomerates produced with additives and binders are found to be 35 wt. % (directly measured after agglomeration formation) and the agglomerates after stabilization for 7 days have a water content of around 5 wt. %.

Even though pellet production with CMC as additive is highly successful, a loss of the fertilizing efficiency up to 50 % occurred. To solve this problem of loosing fertilizing efficiency, the innovative encapsulation process is carried out. In the direct encapsulation the biogas residues are encapsulated with gelatin and PLA foils. The thus produced capsules contain 100 % of the solid and liquid phase and have 100 % fertilizing efficiency, through which the challenges in handling of the biogas residues are taken care off.

The gelatin and PLA capsules have low abrasion values (figure 75) but also display low strength. These results make the capsules not easily eligible for transport and storage and are thus not considered a good option as solid fertilizers.

To achieve good results for abrasion and strength in capsules, indirect encapsulation with alginate is carried out after agglomeration of biogas residues with additives and binders. This is carried out for biogas residue pellets with 2.5 wt. % CMC as this mixture yields the highest nitrogen content of approximately 50 %.

Through the means of indirect encapsulation the nitrogen release of the capsules is belated as the alginate capsule needs to be diluted before the release of the fertilizing effects of the inside pelletized biogas residues. The nitrogen release can be further time delayed through multilayer encapsulation and multi-compartment encapsulations.

The indirect encapsulation (multilayer, multi-compartment) can be used at the field as a combined long term fertilizer, reducing the need for several fertilizer applications (separate application of solid and liquid phases). The fertilizers reach the soil segmented over a long time period. Through the usage of solid encapsulated fertilizers compared to liquid fertilizers, the risk of ground water and water bodies' contamination can be reduced.

7.4 Open questions / outlook

Industrial residues: Black liquors (lignin)

The production of lignin agglomerates with the help of the innovative patented process is only carried out on a laboratory scale, which will be undergoing an up-scaling from laboratory scale to pilot plant or demonstration scale by working together with the company Gebrüder Lödige Maschinenbau GmbH. The up-scaling process also tries to substitute the spray granulator with pelleting mixers.

Further research will also be carried out on the preparation and production of biomass-mix pellets with lignin and other biogenous residues materials having high chlorine, high sulphur and high ash contents (for example straw, biogas residues, etc.).

Biotechnological (Biogas) residues

The production of various agglomerates with i) additives, ii) binders, iii) after dewatering and the different capsules are only carried on laboratory scale. The results of the analysis show that the produced agglomerates are better in comparison to the conventionally produced agglomerates. The real time fertilization efficiency will be tested in green house and in field in the near future. The results from laboratory scale will be transferred to demonstration scale and will be tested in the field.

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9. Appendix

9.1 Agricultural residues: Cereal Straws

Table 15: Abrasion of pellets and their blends

ASAE S269.4									
Water Content (%)	Rye straw		Wheat straw		P1	P2	AC	LC1	LC2
	HM	EX	HM	EX					
14.0000	14.0000	10.0000	12.0000	19.0000	13.0000				
15.0000	8.4000	7.6000	7.8000	12.1000	11.0000	13.0000			
16.0000	4.9000	5.4000	4.8500	9.8000	9.4000	10.3000	3.6500	4.3000	4.8000
17.0000	4.2000	2.6000	4.2000	5.9000	8.0000	8.7000	3.4200	3.2000	3.1000
18.0000	5.0000	5.1000	4.0000	3.0000	10.0000	9.4000	3.4800	2.8000	2.1000
19.0000	9.0000	8.4000	8.1000	6.4000	13.6000	12.0000	3.6000	3.6000	5.1000
20.0000	18.0000	9.7000	16.0000	10.1000	16.8000	15.0000	8.2200	5.8000	8.4000
SS 187120									
14.0000	5.0000	3.5000	4.0000	5.9000	4.4000				
15.0000	2.9000	2.5000	2.6000	3.8700	3.7000	4.1000			
16.0000	1.7000	1.8500	1.6000	3.3000	3.0000	3.1000	1.2000	1.4300	1.6000
17.0000	1.4000	0.9300	1.4000	1.9000	2.4000	2.8000	1.1200	1.0500	1.0400
18.0000	1.8000	1.7000	1.2000	0.9000	3.4000	3.1000	1.1000	0.9400	0.7000
19.0000	3.0000	2.8000	2.3000	2.1000	4.4000	3.6000	1.2000	1.2000	1.3000
20.0000	6.0000	3.2300	4.9000	3.4000	4.8000	4.3000	1.8000	1.5000	2.1000

Table 15: Abrasion of pellets and their blends (Continuation)

SS 187120 + 1 Baffle									
Water Content (%)	Rye straw		Wheat straw		P1	P2	AC	LC1	LC2
	HM	EX	HM	EX					
14.0000	6.0000	5.2000	7.2000	5.8000	7.5000				
15.0000	4.3000	3.8000	5.6000	4.8000	5.9000	7.5000			
16.0000	2.3000	2.6000	4.2000	3.7000	4.7000	5.1000	1.9000	2.1500	2.4000
17.0000	1.9000	1.3000	3.1000	2.6000	4.0000	4.6000	1.7000	1.6000	1.5600
18.0000	2.4000	2.4000	2.0000	1.5000	5.0000	4.5000	1.6000	1.3500	1.0600
19.0000	4.0000	4.1000	2.9000	2.4000	6.3000	5.8000	1.8000	1.8000	2.5900
20.0000	7.5000	4.9000	4.3000	4.0000	8.3000	7.5000	2.9000	2.7000	3.3500
SS 187120 + 2 Baffles									
14.0000	9.7000	6.7000	8.0000	7.3000	8.8000				
15.0000	5.4000	4.8000	5.6000	5.4000	7.8000	7.6000			
16.0000	4.8000	3.7000	3.8000	3.3000	6.0000	5.9000	2.4000	2.9000	3.1000
17.0000	3.7000	1.9000	2.9000	2.7000	4.7000	5.1000	2.1000	2.1000	2.0000
18.0000	4.5000	3.0600	2.1000	1.8000	5.8000	6.0000	1.9000	1.9000	1.5000
19.0000	5.9000	4.9000	4.1000	3.9000	7.9000	6.9000	2.3000	2.5000	2.6000
20.0000	11.3000	6.4000	8.7000	6.8000	9.6000	7.8000	3.1000	2.9000	3.2000

Table 16: Strength of pellets and their blends

Diametrical strength									
Water Content (%)	Rye straw		Wheat straw		P1	P2	AC	LC1	LC2
	HM	EX	HM	EX					
14.0000	160.0000	221.0000	180.0000	213.0000	175.0000	157.0000			
15.0000	306.0000	480.0000	228.0000	458.0000	180.0000	160.0000			
16.0000	480.0000	565.0000	319.0000	520.0000	200.0000	195.0000	560.0000	628.0000	524.0000
17.0000	543.0000	627.0000	490.0000	591.0000	230.0000	219.0000	605.0000	735.0000	703.0000
18.0000	450.0000	570.0000	550.0000	605.0000	195.0000	189.0000	600.0000	825.0000	745.0000
19.0000	335.0000	467.0000	456.0000	429.0000	172.0000	165.0000	603.0000	605.0000	695.0000
20.0000	210.0000	306.0000	346.0000	287.0000	170.0000	162.0000	485.0000	485.0000	509.0000
Point Force									
14.0000	26.6667	36.8333	30.0000	35.5000	29.1667				
15.0000	51.0000	80.0000	38.0000	76.3333	30.0000	26.6667			
16.0000	80.0000	94.1667	53.1667	86.6667	33.3333	32.5000	93.3333	104.6667	87.3333
17.0000	90.5000	104.5000	81.6667	98.5000	38.3333	36.5000	100.8333	122.5000	117.1667
18.0000	75.0000	95.0000	91.6667	100.8333	32.5000	31.5000	100.0000	137.5000	124.1667
19.0000	55.8333	77.8333	76.0000	71.5000	28.6667	27.5000	100.5000	100.8333	115.8333
20.0000	35.0000	51.0000	57.6667	47.8333	28.3333	27.0000	80.8333	80.8333	84.8333
Three Point Force									
14.0000	4.4444	6.1389	5.0000	5.9167	4.8611				
15.0000	8.5000	13.3333	6.3333	12.7222	5.0000	4.4444			
16.0000	13.3333	15.6944	8.8611	14.4444	5.5556	5.4167	15.5556	17.4444	14.5556
17.0000	15.0800	17.4200	14.1000	15.3200	6.3900	6.0800	16.8060	19.5400	18.2900
18.0000	13.1000	14.8900	15.2800	16.8100	5.1200	5.2500	16.7000	22.9160	20.6940
19.0000	9.3056	12.9722	12.6667	11.9167	4.7778	4.5833	16.7500	16.8056	19.3056
20.0000	5.8333	8.5000	9.6111	7.9722	4.7222	4.5000	13.4722	13.4722	14.1389

Table 16: Strength of pellets and their blends (Continuation)

Impact Resistance									
Water Content (%)	Rye straw		Wheat straw		P1	P2	AC	LC1	LC2
	HM	EX	HM	EX					
14.0000	0.3712	0.5128	0.4176	0.0000	0.4060				
15.0000	0.7100	1.1137	0.5290	1.0626	0.4176	0.3712			
16.0000	1.1137	1.3109	0.7401	1.2065	0.4640	0.4524	1.2993	1.4571	1.2158
17.0000	1.2599	1.4548	1.1369	1.3712	0.5336	0.5081	1.4037	1.7053	1.6311
18.0000	1.0441	1.3225	1.2761	1.4037	0.4524	0.4385	1.3921	1.9142	1.7285
19.0000	0.7773	1.0835	1.0580	0.9954	0.3991	0.3828	1.3991	1.4037	1.6125
20.0000	0.4872	0.7100	0.8028	0.6659	0.3944	0.3759	1.1253	1.1253	1.1810

9.2 Industrial residues: Black liqours

Table 17: Lignin yield after acidification of liquid liqour at varying temperatures with varying acid concentrations.

H_2SO_4 Acid Concentration (ml ml^{-1})	Yield at different temperatures			
	20 °C	50 °C	70 °C	100 °C
0.0025	3.8500	11.7700	16.4900	12.2000
0.0100	19.5700	32.3400	30.4400	24.8700
0.0300	33.2000	56.8900	55.6000	56.2800

Table 18: Density and strength of the produced granules at different reactor temperatures before and after acid treatment

Temp. (°C)	Density (Kg m^{-3})	Strength (N mm^{-2})	Strength after acid treatment (N mm^{-2})		
			Ca-LS	Na-LS	KL
80.0000	664.3459 (18.74)	2.3349 (0.63)	2.01 (1.78)	6.02 (4.52)	--
100.0000	630.0000 (19.79)	2.0601 (0.92)	2.03 (1.85)	5.89 (4.60)	0.12 (0.01)
120.0000	608.0000 (18.38)	1.8505 (0.85)	--	--	--
140.0000	579.8158 (6.82)	0.9180 (0.65)	--	--	--
160.0000	533.4497 (35.84)	0.8617 (0.43)	--	--	--
180.0000	496.8795 (7.25)	0.5919 (0.48)	--	--	--

Table 19: Evaporation energy and throughput of the spray granulator

Temperature (°C)	Evaporations energy (MJ h^{-1}) / (MJ kg^{-1})	Throughput (kg)	Energy at 80 °C	Energy at 100 °C
0.0000	0.0000	0.5000	19.6000	25.2000
21.0000	0.0000	1.0000	9.8300	12.6000
60.0000	9.8300	2.0000	4.9100	6.3000
100.0000	12.6000	3.0000	3.2800	4.2000
150.0000	18.3000	4.0000	2.4500	3.2000
220.0000	23.8600	5.0000	1.8500	2.5200
		6.0000	1.6400	2.1000

Table 20: pH changes with respect to increasing mass of granules in acid treatment.

Granules Mass (g)	pH value changes		
	Ca-LS (H_2SO_4)	Na-LS (H_2SO_4)	KL (CH_3COOH)
0.0000	0.0000	0.0000	1.9900
5.0000	0.0000	0.0000	3.7400
10.0000	0.0000	0.0000	4.1500
15.0000	0.0000	0.0000	4.2400
20.0000	0.0200	0.0000	4.4300
25.0000		0.4000	4.6700
30.0000		0.6000	4.9100
35.0000			5.0200
40.0000			5.1900
45.0000			5.2400
50.0000			5.6000
55.0000			5.6400
60.0000			5.8500

Table 21: Pore sizes of granules and their liquid holding capacities.

Variants	Pore sizes (µm)	Liquid holding capacity (h)				
		0	1	2	50	100
Ca-LS	0.141 (0.072)	100 %	65 %	35 %	0.0 %	0.0 %
Na-LS	0.140 (0.078)	100 %	93 %	89 %	15 %	0.0 %
KL	0.223 (0.132)	--- Not applicable ---				

9.3 Biotechnological residues

Table 22: Dewatering of biogas residues with respect to time.

Time (min.)	Before Communition (g)	After Communition (g)	
		10 mm Sieve	6 mm Sieve
0.0000	0.0000	0.0000	0.0000
5.0000	225.0000	159.0667	66.2000
10.0000	360.0000	241.2667	119.9667
15.0000	452.0000	289.7667	163.6667
20.0000	518.0000	321.4000	197.6333
25.0000	566.0000	342.2333	224.4667
30.0000	609.0000	364.0000	245.4000
35.0000	636.0000	375.0000	261.3333
40.0000	656.0000	384.0000	272.6333
45.0000	676.0000	396.0000	280.5333
50.0000	688.0000	403.0000	285.9333
55.0000	702.0000	413.0000	289.6000
60.0000	712.0000	420.5000	292.1667
65.0000	713.0000	420.9000	293.4333
70.0000	714.0000	421.5000	293.9333

Table 23: Abrasion and Strength of biogas residues.

Variants		Abrasion (%)	Strength (N)
Lime	L1	8.0000	0.0000
	L2	6.6800	0.0000
	L3	6.6800	20.1100
	L4	7.2900	8.6200
	L5	7.8600	10.2500
	L6	12.1000	5.5600
	L7	12.2600	13.1200
	L8	11.9000	7.7600
	L9	11.4400	6.4500
	L10	16.8000	0.0000
	L11	15.9000	0.0000
	L12	16.8000	0.0000
Starch	S1	7.6000	17.2500
	S2	4.2000	24.0400
	S3	10.3000	11.3100
Gelatin	G1	16.3000	8.3000
	G2	12.4000	13.8100
	G3	11.9000	13.9700
CMC	CMC1	3.9000	77.4800
	CMC2	3.1000	86.6200
	CMC3	1.9000	92.0000
Alginate-L	AL1	1.8500	3.6900
Li-Granule	LG1	0.9000	1.8000
	LG2	0.5000	2.1000
Alginate	AL-S1	8.5000	9.4100
	AL-S2	2.4500	40.1900
	AL-S3	2.1000	48.4200
	AL-G1	10.1000	17.2500
	AL-G2	7.6000	24.0400
	AL-G3	14.6000	11.3100
	AL-CMC1	1.6400	98.0000
	AL-CMC2	1.3500	126.0000
	AL-CMC3	0.8600	154.0000
	AL-LG1	0.8000	1.9000
	AL-LG2	0.3000	2.2000
Gel. Capsules	GC1	2.4500	7.2000
	GC2	2.7900	4.9000
	GC3	2.1000	8.5000
PLA	PLA	1.56	3.3000
Centrifuge	C1	4.4600	9086.3400
	C2	1.3800	9902.5200